LOCALISED CORROSION OF STAINLESS STEELS – LIMITS AND MECHANISMS

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Abstract

Pitting, crevice corrosion and stress corrosion cracking are often regarded separately, with various more or less standardised tests being used to rank the relative performance of different steel grades. However, the processes are interlinked by the common themes of passivity and breakdown. From an engineering point of view it is also necessary to regard the localised corrosion processes together in order to avoid component failure.

This paper discusses the concept of defining limiting conditions for pitting, crevice corrosion and stress corrosion cracking in terms of the environmental parameters temperature, potential and chloride concentration. It also considers the effect of crevices and loading method in the light of the current understanding of the underlying mechanisms.

Introduction

Localised corrosion, particularly in chloride environments is the "Achilles heel" of stainless steels – in other words, it is the weak point in an otherwise extremely robust constitution. Pitting, crevice corrosion or stress corrosion cracking can lead to leakage of a tube or vessel even though the majority of the surface shows no signs of corrosion.

There are numerous standardised tests for pitting, crevice corrosion and stress corrosion cracking of stainless steels. These include the methodology descriptions in ISO 7539 [1]⁻ for stress corrosion cracking and the standardised tests methods for pitting in ASTM G61 [2] and ASTM G150 [3]. However the available tests are primarily used for comparative purposes – to rank the behaviour of different alloy grades in relation to one another. This is not always useful when the question is one of selecting the right material for a particular environment. The design against localised corrosion therefore still largely has to rely on practical experience from field testing and industrial installations and existing data from laboratory testing serve primarily as guide lines.

In terms of critical variables, it is well recognised that the susceptibility of stainless steels to pitting, crevice corrosion and stress corrosion cracking increases with temperature and with the aggressivity of the corrosive medium. The idea of engineering diagrams based on pitting potential measurements was presented in 1989 [4]. The concept of a critical temperature for pitting based on a large number of potentiodynamic pitting potential measurements at different temperatures was introduced about the same time [5] and some typical data shown in Figure 1. The concept of raising the temperature at a constant potential in order to determine the critical pitting temperature from only a single specimen was adopted in 1997.



Figure 1. Potentiodynamic determination of CPT from Qvarfort [5] showing abrupt transition between transpassive corrosion and pitting as measurements are made at successively higher temperatures

If variation in chloride concentration is added to Figure1, then a three dimensional diagram illustrated schematically in Figure 2. is obtained. The area closest to the origin represents the "safe" region in which pitting does not occur. Increasing the temperature, potential or chloride concentration increases the risk for pitting until the boundary to the pitting regime is crossed. Strictly speaking, the upper limit in potential may be defined by transpassive corrosion, or dissolution of the passive film, rather than actual localised formation of pits. Introduction of further variables yields a multidimensional volume, which is further complicated when the boundaries for stress corrosion cracking and crevice corrosion are superimposed. For the sake of simplicity, this combined concept is illustrated in two dimensions in Figure 3. This approach is currently being evaluated within the RFCS project CORINOX "Avoiding catastrophic corrosion failure of stainless steels" which will run until 2010.





Figure 2. Schematic illustration of the limiting conditions for pitting. The volume close to the origin is that in which no pitting occurs. The upper bound in potential may be defined by transpassive dissolution, the curved line by pitting.

Figure 3. Combined fields for different types of corrosion and effect of experimental variables.

Experimental

Test results presented in this work have been taken from a variety of investigations using the test methods described in the Introduction. These include pitting potential determination with a scan rate of 20mV/min, evaluated at 250μ A/cm², measurement of the critical pitting temperature with a ramp of 1°C/min and evaluation when the current density exceeded 100 μ A/cm² for 60s. Crevice corrosion was tested using a method similar to ASTM G150 with a creviced specimen as described in [6], a slower temperature ramp of 0.1°C/min and evaluation when the corrosion current exceeded 10 μ A for 60s. For stress corrosion cracking U-bend specimens with dimensions L=130mm; w=13 mm; t=2mm bent over a 25mm diameter mandrel or slow strain rate testing at 10⁻⁶s⁻¹was employed. Typical compositions of the steels investigated are given in Table 1.

Table 1. Typical compositions of stainless steels referred to in this work

| EN | С | N | Cr | Ni | Mo |
|--------|------|------|------|------|-----|
| 1.4404 | 0.02 | | 17.2 | 10.1 | 2.1 |
| 1.4438 | 0.02 | | 18.2 | 13.7 | 3.1 |
| 1.4462 | 0.02 | 0.17 | 22 | 5.7 | 3.1 |
| 1.4410 | 0.02 | 0.27 | 25 | 7 | 4 |
| 1.4547 | 0.01 | 0.20 | 20 | 18 | 6.1 |

Results and discussion

Pitting

Pitting potentials typically exhibit a broad distribution, which has been related by Baroux [8] and others to the stochastic nature of the initiation process. Data in Figure 4a) for 1.4462 in 1M NaCl show standard deviations in excess of 100mV which are by no means abnormal. In contrast, critical pitting temperatures, such as the data in Figure 4b), normally show much narrower scatter. This has been rationalised by Newman [9] as reflecting the dominance of the propagation process and the steep temperature dependence of the limiting current for repassivation.



Figure 4. (a) (b) Pitting potentials and critical pitting temperatures for 1.4462 from [7]. (c) Comparison of data from a)and b) shows good agreement in terms of limiting conditions for pitting (d) Data from [10] showing discrepancy between pitting potential and CPT in saturated MgCl₂(pH~3)

A comparison of CPT and pitting potential data in Figure 4c) nevertheless shows good agreement in terms of limiting conditions and definition of the pitting/no pitting boundary for 1.4462 in 1M NaCl. However, this level of agreement is not universal. Figure 4d) shows results from ongoing work in which the same type of comparison has been made for a saturated MgCl₂ solution. This is a rather different type of electrolyte, with a low pH due to the hydrolysis reactions at high metal ion activities [9], and shows less consistent behaviour. There is a large difference which has at least two possible explanations. One is that the CPT measurement is of longer duration, so the passive film has been conditioned or toughened during the slow temperature ramp, the other is that there may be a quasi-active potential region at around 0mV at higher temperatures which can cause attack during pitting potential measurements. Definition of boundary conditions should in this case be based on the most conservative data, in this case pitting potentials. The difference also underlines that the time factor is of importance, and indicates that longer term exposure testing is advisable for firmer definition of pitting boundary conditions.

A comprehensive investigation of the critical pitting temperature for 1.4404 has been carried out in MgCl₂ solutions with similar concentrations to NaCl. Figure 5 shows data plotted in two different dimensions of the multicomponent space. The two electrolytes show remarkably good agreement and also the same trends of a shift in the pitting boundary towards the origin by an increase in either concentration or potential. The effect of potential is larger than expected against the background of the concept of a "potential independent CPT" in ASTM G150, for example a drop in the applied potential from 700mV SCE to 300mV SCE increases the CPT from 19°C to 40-45°C . In a similar vein, decreasing the chloride concentration increases the CPT e.g. by ~8°C when the chloride concentration is reduced from 2M to 1M at 500mV. This effect of concentration becomes more pronounced at lower potentials. The mechanistic rationale behind these trends is open to speculation, but it appears reasonable that a higher temperature is required to maintain the high current density necessary for pit propagation in a milder environment.



Figure 5. Effect of chloride concentration and potential on CPT for 1.4404 from [11] and comparison with pitting potential measurements in 1M chloride solution (crosses). The solution pH was 5-6 for both $MgCl_2$ and NaCl solutions over the concentration range investigated.

Crevice corrosion

The presence of a crevice accelerates the onset of localised corrosion because the restricted geometry allows more rapid establishment of an aggressive electrolyte [12]. Consequences in terms of limiting conditions are illustrated by the CPT and CCT measurements for 1.4462 in Figure 6. In this case the presence of a crevice has decreased the critical temperature by 35°C. It cannot be emphasised too much in this context that crevice width and length both have a strong effect so establishment of application limits should involve comparison of crevice geometries and identification of the worst possible case to give a conservative limit.



Figure 6. Temperature dependence of CPT and CCT for 1.4462 in 1M NaCl, including some data from [6]. Note that this is a different heat of 1.4462 with a slightly higher CPT than that in Figure 4.

Stress corrosion cracking

The concept of limiting conditions for stress corrosion cracking was introduced in [13] and is illustrated by some examples in Figure 7.



Figure 7a-b) U-bend (triangles) and SSRT results for 1.4462 in CaCl₂ and LiCl from [13] c) Compilation of data from [14] d) Results of practical experience and constant load tests from [15]

These examples illustrate the same trend as for pitting, namely the "safe zone" at low temperatures and chloride contents, and a fairly well-defined boundary defining the SCC region. The effect of potential remains to be explored, but is liable to be a complicated question, in view of many indications that crack propensity is highest in bands of potential relating to instable passivity. The data underline several important features. Firstly Figure 7a) shows that testing in 10M CaCl₂ at 100°C gave cracking in SSRT but not in U-bend tests. This is a general trend for duplex steels [15], while the opposite situation is observed for austentic steels. The underlying mechanism for this effect is still under investigation, but appears to be related to the mechanical-electrochemical interaction between phases [14] and the larger degree of relaxation in constant deflection in austenitic steels compared to duplex [15]. Secondly, a comparison between Figure 7a) and b) demonstrates that the cation can be significant, with lower SCC boundaries in the more aggressive LiCl solution. Finally Figure 7c) shows the same important point about the detrimental effect of crevices as seen in Figure 4. In this case the SCC temperature decreased by

130°C due to the presence of a crevice between double U-bend specimens. Design to avoid critical crevice geometries is thus of paramount importance in environments where there is a risk of SCC.

Conclusions

Limiting conditions for the occurrence of pitting and stress corrosion cracking of stainless steels can be defined in terms of chloride concentration, temperature and potential. In both cases the presence of a crevice geometry radically decreases the "safe zone" in which localised corrosion can be avoided. This approach represents a step away from simple alloy ranking and towards design data which will facilitate use of stainless steels in new application areas.

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ELECTROCHEMICAL METHOD TO EVALUATE THE STAINLESS STEEL INTERGRANULAR CORROSION RESISTANCE

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Abstract

By means of electrochemical techniques, it has been possible to quantify the stainless steel intergranular corrosion behaviour. The potentiodynamic reactivation method has been employed. The typical EN 1.4301 and EN 1.4307 (high and low carbon) as test materials have been selected. The TTS (Time – Temperature – Sensitivity) diagrams (Temperature range: 450 °C-1000 °C; Time range: 0.5 - 60000 minutes) by electrochemical tests, ASTM A 262 Practice A, ASTM A 262 Practice E and weight loss tests were performed. The correlation between the different techniques enabled to obtain the "Q" value and to establish the relationship with traditional tests. The "non-acceptable" samples by ASTM A 262 Practice E that present "Ditch Structure" by ASTM A 262 Practice A, have a "Q" value higher than 0.01 in the electrochemical tests. The samples that present "Q < 0.01" in all cases are non-sensitized samples.

Introduction

Nowadays, the stainless steels intergranular corrosion evaluation is made by traditional testing techniques. The new electric measurement techniques have advanced in order to develop methods that are able to quantify the sensitization levels. The adjustment of these electrochemical methods and the correlation with the traditional tests are of the outmost importance in order to improve knowledge on the intergranular corrosion of stainless steels. In this paper, a new method developed by means of electrochemical techniques will be described that it is able to quantify the austenitic stainless steel intergranular corrosion behaviour. EN 1.4301 and EN 1.4307 steels have been used. After different thermal treatments the samples have been tested in order to determine their intergranular corrosion behaviour by electrical measurements. The "Q" value has been obtained.

All the samples were tested traditionally according to ASTM A 262 Practice A and Practice E and determining the weight loss in acid solutions. The comparison between these different techniques will allow to establish the correlation between the "Q" value obtained by electrochemical methods and the others experimental techniques.

Materials

For the present tests, austenitic stainless steels EN 1.4301 and EN 1.4307 (in 2 mm thickness) cold rolled, annealed and pickled were selected. The chemical composition is given in Table 1.

Table 1. Chemical composition of the steels

| | | % in weight | | | | | | | | | | |
|-----------|-------|-------------|------|-------|------|------|-------|-------|-------|-------|-------|--|
| | С | Si | Mn | Cr | Ni | Mo | Р | Ti | Nb | S | Ν | |
| EN 1.4301 | 0.056 | 0.47 | 1.86 | 18.06 | 8.27 | 0.27 | 0.034 | 0.007 | 0.090 | 0.001 | 0.048 | |
| EN 1.4307 | 0.028 | 0.34 | 1.86 | 18.20 | 8.12 | 0.25 | 0.032 | 0.005 | 0.006 | 0.001 | 0.072 | |

Thermal treatment

In order to obtain the TTS diagrams, the samples were submitted to different thermal treatments before the intergranular corrosion tests. Temperature range between 450-1000 °C and time between 0.5-60000 minutes have been used.

ASTM A 262 Practice A

After thermal treatment, a transversal section of the sample was prepared. By means of electrolytic attack in 10% oxalic acid solution $(1 \text{ A/cm}^2 - 1.5 \text{ minutes})$ the samples could be characterized into Step, Dual and Ditch Structures (see Figures 1, 2 and 3). It is easy to observe that the stainless steel with the low carbon content needs much more time in thermal treatment before showing ditch structures



The TTS diagrams corresponding to the Practice A are plotted in Figures 4 and 5.





Figure 5. TTS for EN 1.4307, Practice A

ASTM A 262 Practice E

On the heat treated samples with pickled or polished surfaces, the samples were tested in a boiling 6 % $CuSO_4 - 16$ % H_2SO_4 solution for 24 hours. Electrolytic copper was in contact with the samples during the tests. At least three samples were tested for each thermal treatment.

A 180° bending test was used to determine ACCEPTABLE / NON ACCEPTABLE samples (Figures 6 and 7).



Figure 6. Acceptable

Figure 7. Non acceptable

The summary of the tests results are shown in the TTS diagrams in Figures 8 and 9.





Figure 9. TTS for EN-1.4307, Practice-E

The sensitization appears at 750°C / 15min for EN 1.4301, but not for the low carbon material.

The corrosion rate (Vcorr) was evaluated by weighting of the samples before and after the tests. Vcorr (mm/month) = 7289.8 W / (A x.d x.t) where W = Weight loss (g) A = samples Area (cm²) d = Density (g/cm³) t = immersion Time (hours)

The corrosion rate for EN 1.4301 and EN 1.4307 is shown in Figure 10 and 11, respectively.



Figure 10. Corrosion rate for-EN 1.4301

Figure 11. Corrosion rate for-EN 1.4307

10000

100000

The low temperature thermal treatment shows an increase of the corrosion rate with time. At 650°C a decrease in the corrosion rate with the treatment time is observed beyond 3000 minutes for EN 1.4301 and 6000 minutes for EN 1.4307.

Electrochemical methods

The electrochemical tests were carried out in a flat cell (Figure 12). The electrolyte was a 0.5M $H_2SO_4 + 0.01M$ KSCN solution at 25°C. The sample surface was polished to 600#.

15 minutes before and during all the tests, the solution was nitrogen burbled (0,8l/min).

The polarization curves were obtained by means of cyclic polarization tests. The initial potential was -300 mV vs open circuit and the inversion potential was 300mV vs SCE. At a final potential of 0 mV versus open circuit, the test was stopped. The polarization rate was 1.7 mV/s.

The sensitization degree was measured by means of the activation and reactivation current densities.



Figure 12. Flat cell

The "Q" value obtained for all the thermal treatments for the both stainless steels are plotted in Figures 13 and 14.





Figure 14. "Q" -EN 1.4307

The temperatures that affect the "Q" values considerably are 550°C, 650°C and 750°C. For the steel grade EN 1.4301 it is clear that at temperature of 750°C sensitization occurs, at the rate decreasing with the time. At 650°C the "Q" value increases with the time of thermal treatment

and at 550°C the sensitization appears after 3000 minutes. In the case of low carbon stainless steel, it is observed that the most critical sensitization temperature is 650°C, followed by 550°C.

Results

All the results obtained by the four experimental techniques have been included in the same figure for comparison. In TTS diagrams (Temperature-Time-Susceptibility to intergranular corrosion) it is possible to make comparisons between the relative behaviour of samples recorded by the different methods.

| EN 1.4301 Temperature | I | | | | | | | | | | | | |
|----------------------------|---------------------------|----|------------|------|------|-----|---------|---------|---------|--------------------|----------------------|----------|---------|
| (in °C) | | | | | | | | | | | | | |
| 1000 | 1 | 1 | 1 | 1 | | | | | | | | | |
| 950 | 1 | 1 | 1 | 1 | 1 1 | | 1 | | | | | | |
| 900 | 1 | 1 | 1 | 1 | 1 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 |
| 850 | 1 | 1 | 1 | 1 | 1 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 |
| 750 | | 1 | 1 | 1 | 2 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 |
| 650 | | | 1 | 1 | 1 1 | 2 | 2 | 2 | 3 | 3 | 3 | 2 | 2 |
| 550 | | | | 1 | 1 1 | 1 | 1 | 1 | 2 | 2 | 3 | 4 | 4 |
| 450 | | | | 1 | 1 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 3 |
| Time | 0.5 | 1 | 5 | 15 . | 30 4 | 5 6 | 0 12 | 0 30 | 0 60 | 0 300 | 0 600 | 0 3000 | 0 60000 |
| (in min) | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| EN 1.4307 | | | | | | | | | | | | | |
| Temperature | | | | | | | | | | | | | |
| (in °C) | | | - | 1 | 1 | - | 1 | 1 | | | 1 | | |
| 1000 | | | - | | | | | | | | | | |
| 950 | | | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| 900 | | | 2 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 |
| 750 | | 1 | 1 | 1 | | | 2 | 1 | 2 | 1 7 | 1 | 1 | 2 |
| 650 | | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | - 2 | <u>າ</u> | 1 |
| 550 | | | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 3 | 2 | 3 |
| 450 | | | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 |
| Time | 05 1 | 5 | 15 | 30 | 45 | 60 | 120 | 300 | 600 | 3000 | 6000 | 30000 | 60000 |
| (in min) | 0.0 | U | 10 | 20 | | 00 | 120 | 200 | 000 | 2000 | 0000 | 20000 | 00000 |
| | | | | | | | | | | | | | |
| Electrochemical Practice-A | | | | | | Pı | actice- | E | | Vco | rr | | |
| | | | | | | | | | | | | | |
| | Q<0.00 | 01 | [| | Step | | |] Non a | aceptab | le 1 | V _{corr} <0 | 0.01 | |
| 0.0001 | <u><</u> Q<0.00 | 1 | Į. | | | | | | 20 | $0.01 \leq V_{co}$ | rr<0.1 | | |
| | <u>-</u> Q<0.01 -0-0-1 | | ۳ <u>6</u> | 8888 | | | | | 3 | $0.1 \ge V_{co}$ | m<1.0 V | >1.0 | |
| 0.01 | $2V \setminus 0.1$ | | | | | | | | | | -/ | - | |

Conclusions

- It is checked that certain Ditch Structure are "Acceptable" by Practice E. All the "Non Acceptable" samples present Ditch structure and the "Q" value is higher than 0.01.
- The Dual Structure presents "Q" values between 0.0001 and 0.01.
- When "Q" value is lower than 0.0001, the etched structure is classified as Step.
- Corrosion rate higher than 1.0mm/month shows "Non-Acceptable" structure.

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ATMOSPHERIC STRESS CORROSION CRACKING OF STAINLESS STEELS IN SWIMMING POOL ENVIRONMENTS

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Abstract

Stainless steels are used for three main types of swimming pool equipment: in the pool water conditioning plant, equipment immersed in pool water and equipment exposed to swimming pool atmospheres. Several cases of ceiling collapses and of other failed elements in swimming pool halls have been reported. It was found that the collapses were caused by stress corrosion cracking (SCC) of stainless steel load bearing components subject to tensile stress. In all reported cases the failed parts, were made of stainless steel grades EN 1.4301, EN 1.4401, or similar steel grades. In order to determine the likelihood of atmospheric SCC for different stainless steel grades for swimming pool atmospheric conditions, systematic laboratory tests and field tests were carried out.

Introduction

Several cases of ceiling collapses in swimming pool halls have been reported [1,2,3]. For example, in Uster, Switzerland, 1985, where a concrete suspended ceiling in a 13-year old indoor swimming pool collapsed [1,4,5]. In general, there is no critical corrosion problem connected with stainless steel equipment in pool water conditioning plats or in immersed conditions [6]. However, problems occurred with the equipment exposed to swimming pool atmospheres, particularly with the safety-relevant accessories subject to external or internal tensile stress. It was found that most of the collapses were associated with the failure of load bearing components and the cause was stress corrosion cracking (SCC). In all reported cases, the failed parts were made of austenitic stainless steel grades EN 1.4301, EN 1.4401, or similar. Acid chloride deposits were found on the surface of damaged parts, with typical pH values of 3-4. Considering cat-ions, relatively large quantities of calcium and sometimes also magnesium were often detected [7,8,9,10,11]. In most cases, unexpected SCC was observed in conjunction with pitting and cracks originating from the bottom of corrosion pits [9,12]. All the failed parts were coldworked and/or were subject to additional stress or work hardening on installation or in service. The temperature in the swimming pool buildings was about 30°C, which is in contradiction with the general corrosion literature regarding chloride induced stress corrosion cracking of stainless steels that considers SCC to occur at temperatures exceeding 50-60°C.

Following corrosion studies disclosed that there are two specific conditions leading to lowtemperature SCC. For example, at pH from -0.5 to 0.5 at high chloride concentration from 0.5 to 5 M caused SCC of austenitic stainless steel at temperatures below 60 °C[1,8,10]. Since stainless steels were under these conditions corroding in the active state, this mode of SCC was accompanied by considerable general corrosion rate, [1,10,12,13,14,15]. By increasing the concentration of chloride, the critical hydrogen ion (H⁺) concentration leading to SCC decreased. Both too high and too low acidity led to another type of corrosion attack, e.g. pitting or crevice corrosion [15]. Secondly, SCC was observed in environments with extremely high chloride levels over 20 wt. % and at around the relative humidity (RH) corresponding to the point of deliquescence [12,15]. Such chloride concentration requires the presence of chloride salts of sufficiently high solubility, e.g. calcium or magnesium chlorides on the metal surface, as their saturated concentrations significantly exceed that of sodium chloride. A high chloride concentration is the only prerequisite for inducing this type of SCC and highly acidic conditions are generally not necessary. The susceptible stainless steels are under these conditions very probably in a passive state [7,10,12,15]. The results of examinations of failed stainless steel segments indicated that the passive type of SCC, is more likely connected to the conditions in swimming pool atmospheres [10,12,15].

It was shown by Shoji and Ohnaka [16] that stainless steels covered with chloride salt deposits have the highest susceptibility to SCC when exposed in air at the relative humidity corresponding to the deliquescence point of the chloride salt. This is because the chloride concentration of the solution formed on the surface is the highest at the deliquescence point. Therefore, stainless steels were in this work exposed with MgCl₂ and CaCl₂ deposits over saturated solutions of respective salts in an attempt to find application limits for stainless steels under these circumstances.

Experimental

Materials

Four austenitic and four duplex stainless steel grades were included in the investigation. A list of tested stainless steels with typical chemical compositions and pitting resistance equivalent (PRE) values are given in Table 1.

| Stainless st | teel grade | Microstructure | Typical | l chemica | al comp | osition [%] | Thickness | Total strain |
|-----------------|------------|----------------|---------|----------------|---------|-------------|-----------|--------------|
| EN | Trade Name | (PRE)* | Cr | Cr Ni Mo Other | | [mm] | 3 | |
| 1.4301 S30400 | | A (18) | 18.1 | 8.3 | | | 2.9 | 0.15 |
| 1.4404 | S31600 | A (24) | 17.2 | 10.1 | 2.1 | | 2.9 | 0.15 |
| 1.4539 | 904L | A (37) | 20 | 25 | 4.3 | Cu (1.5) | 1.9 | 0.10 |
| 1.4547 | 254 SMO | A (51) | 20 | 18 | 6.1 | Cu | 2.0 | 0.10 |
| 1.4162 | LDX2101 | D (23) | 22 | 1.5 | 0.3 | Mn (5) | 1.4 | 0.07 |
| 1.4362 | SAF 2304 | D (24) | 23 | 4.8.5 | 0.3 | | 2.0 | 0.10 |
| 1.4462 | 2205 | D (35) | 22 | 5.7 | 3.1 | | 2.0 | 0.10 |
| 1.4410 SAF 2507 | | D (40) | 25 | 7 | 4 | | 3.0 | 0.15 |

Table 1. Typical composition, dimensions and total strain of tested stainless steels

* A austenitic structure, D duplex (austenitic-ferritic) structure; PRE=%Cr + 3.3%Mo + 30%N

U-bend samples were produced according to ASTM G 30-94 with radius of 10 mm. Specimens were cut from sheets parallel to the rolling direction [17]. The surfaces of the samples were exposed in mill finish conditions as delivered, cold rolled. The total strain for stainless steel grades 1.4301 and 1.4404 is at a maximum due to that the thickness is higher for these to grades introducing a higher strain compared to the thinner specimens.

Exposures in swimming pool halls

Three swimming pools were selected for the study, SP 1, SP 2, and SP 3. Data on the swimming pools are summarized in Table 2.

| Swimming | Size of | the pool | | | Chloramin | es in air | Distance from the water level | | |
|----------|----------------|---------------|--------------|-----------------------------|---|--|-------------------------------|-------------------|--|
| pool | Lengt h [m] | Widt h [m] | Depth [m] | Volume [m ³] | As NCl ₃ [mg/m ³] | As Cl ₂ [mg/m ³] | Vertical [m] | Horizontal [m] | |
| SP 1 | 50 | 15 | 1.7 | 1300 | 0.46 | 0.40 | 4.5 | 0.7 | |
| SP 2 | 25 | 10 | 1.3 | 330 | 0.40 | 0.35 | 3.8 | 2.9 | |
| SP 3 | 25 | 10 | 1.6 | 400 | NA | NA | 4.4 | 2.9 | |

Table 2. Parameters of the swimming pools and distance of sample holders from the water level

NA ... data not available

SP 1 is a 50-meter competition swimming pool. Due to a higher number of visitors to this swimming pool, the concentration of free chlorine in the water is kept high (close to 3 ppm of Cl₂) and over-chlorination is applied once a week. Because of a very high chloramine concentration in the pool atmosphere, having caused health problems and limited bather's comfort, a special air cleaning procedure was acquired recently in SP1. SP 2 is a standard 25-meter swimming pool. SP 3 is a pleasure swimming pool situated on the seashore and is fed by seawater.

Results of an audit from November 2003 [18] on the chloramines content in atmospheres of the swimming pools SP 1 and SP 2 are given in Table 2, expressed in the volume concentration of trichloramine as an average of all measurements. The measuring technique did not allow distinguishing trichloramine from mono- and dichloramine and the content of chloramines in air is indicated as Cl_2 . The typical chloramines concentration in a pool atmosphere is 0.3–0.5 mg/m³ as Cl_2 , however, extreme values were reported, up to 1.7 mg/m³ [13]. Sample holders were mounted horizontally at a distance of approximately 5 meters from the pool water level. U-bend samples were placed on the topside of the holder and faced upwards. In addition two zinc (99.8 %) and carbon steel coupons of 50×50 mm, a passive collector for deposits, and a logger for measuring relative humidity and temperature were located on each holder.

Zinc and carbon steel coupons were prepared prior exposure by grinding to 400 grit paper and cleaning in an ultrasonic bath in ethanol for 5 minutes. Stainless steel U-bend samples were cleaned with ethanol before exposure. On completion of the exposures, metal coupons of zinc and carbon steel were pickled in a saturated solution of glycine and Clark solution, respectively. The weight loss was calculated according to ISO 9226 [19].

Sets of U-bend specimens exposed from May 2005 in SP 1, SP3, and SP 3 were removed after 72 weeks in October 2006, together with passive deposit collectors and carbon steel and zinc coupons.

Laboratory experiments

Chloride deposits pre-deposited on the metal surface on stainless steel samples were formed according to a modified procedure used by Shoji and Ohnaka [16]. Six droplets of saturated chloride salt solutions were deposited on top of U-bend samples. All together, $66\pm 2 \mu l$ of the solution was applied on each sample. Details on the chloride surface concentration are given in Table 3.

| Denomi- | Saturated solution | Chloride | Chloride applied on | Surface chloride |
|---------|--------------------|---------------------|---------------------|-----------------------------------|
| nation | | concentration [g/l] | metal [mg] | concentration [g/m ²] |
| Mg | MgCl ₂ | 350 | 23 | 260 |
| Ca | CaCl ₂ | 400 | 26 | 290 |
| Na | NaCl | 190 | 13 | 140 |

Table 3. Surface contamination with droplets of saturated chloride solutions

After exposure, the samples were cleaned in water and examined with a optical light microscope at magnification up to $\times 16$. Selected samples were cut in the longitudinal direction, embedded into resin, polished, and the cross sections were examined with an optical light microscope.

For exposures at 50°C, specimens with magnesium and calcium chloride spots were exposed in desiccators over saturated solutions of magnesium and calcium chloride. The samples were placed in desiccators with respective salts to keep the relative humidity at the deliquescence point and exposed at 50°C for 22 weeks. The relative humidity recorded inside the desiccators was 31 ± 1 % and 17 ± 1 % for MgCl₂ and CaCl₂, respectively. Further test were carried out at a relative humidity of 30 % and at temperatures 20, 30 and 40°C for 10 weeks exposure. A summary of the laboratory test conditions is shown in Table 4.

| Salts | Relative humidity, | Temperatures, | Exposure time, |
|---------------------------------------|--------------------|---------------|----------------|
| | RH % | °C | weeks |
| MgCl ₂ | 31 | 50 | 22 |
| CaCl ₂ | 17 | 50 | 22 |
| MgCl ₂ , CaCl ₂ | 30 | 20, 30, 40 | 10 |
| NaCl/ MgCl ₂ | 30 | 40 | 10 |
| NaCl/ CaCl ₂ | 30 | 40 | 10 |

Table 4. Summary of laboratory experiments with U-bend samples with chloride spots.

Results

Deposition and monitoring the atmospheric environment in swimming pool halls.

The monitored temperature and relative humidity after exposures for 72 weeks, for the three swimming pool atmospheric environments are summarized in Table 5.

Table 5. RH and temperature of swimming pool atmospheres during 72 weeks of exposure.

| Swimming | Relative hun | nidity [%] | | Temperature [°C] | | | | |
|----------|--------------|------------|---------|------------------|---------|---------|--|--|
| pool | Average | Minimum | Maximum | Average | Minimum | Maximum | | |
| SP 1 | 69 | 38 | 95 | 25 | 16 | 35 | | |
| SP 2 | 65 | 34 | 93 | 26 | 14 | 37 | | |
| SP 3 | 52 | 30 | 86 | 28 | 23 | 39 | | |

Table 6. Composition and pH as mean values of soluble deposits on U-bend stainless steel samples after 72 weeks.

| Grade EN | Chloride | Chloride | | Nitrate | | Sulfate | | pН |
|----------|----------|----------|------|---------|------|---------|------|------|
| | [mg] | [%] | [mg] | [%] | [mg] | [%] | [mg] | |
| SP 1 | 2.08 | 68 | 0.03 | 6 | 0.05 | 27 | 2.17 | 5.01 |
| SP 2 | 0.13 | 45 | 0.01 | 1 | 0.07 | 54 | 0.21 | 5.55 |
| SP 3 | 7.37 | 88 | 0.13 | 2 | 0.88 | 11 | 8.38 | 5.57 |

Table 7. Summary of corrosion attack of U-bend samples afte field test for 72 weeks.

| Exposure | Exposure | Stainless | steel grade | (EN) | | | | | _ |
|------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| conditions | [weeks] | 1.4301 | 1.4404 | 1.4539 | 1.4547 | 1.4162 | 1.4362 | 1.4462 | 1.4410 |
| SP 1 | 72 | Pitting | Pitting | <i>n.c.</i> | n.c. | Pitting + | Pitting | <i>n.c.</i> | n.c. |
| SP 2 | 72 | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | n.c. | n.c. |
| SP 3 | 72 | Pitting | Pitting | Pitting | <i>n.c.</i> | Pitting | Pitting | Pitting | <i>n.c.</i> |

n.c.=no corrosion, + Tiny crack

Average results from measurements on two replicates of the carbon steel and zinc coupons are summarized in Table 6. Recalculating the results to one-year exposure, the corrosivity of the atmosphere in SP1 and SP 2, according to ISO 9223 standard [19] can be estimated to class C2.

Based on the corrosion rate of zinc, the corrosivity of the atmosphere in SP 3 was over the limits for the class C5, very high (30–60 g/m² year). Results as mean values from all stainless steel surfaces of dissolved deposits analyzed by ion chromatography are listed in Tables 6. The deposition rate in SP 3 was high and it was assumed that water droplets were the main source of deposits in SP 3.

Corrosion on stainless steel samples after field tests in swimming pool halls

Samples of EN 1.4301, 1.4404, 1.4162, and 1.4362 exposed in SP 1 were covered with corrosion products before cleaning. Corrosion pits were found under the corrosion products. EN 1.4301 was heavily pitted, whereas the other stainless steel grades were pitted in a lower extent. Duplex EN 1.4162 was attacked only in a small area by the edge. Samples exposed in SP 2 were completely free of corrosion. Pitting and etched areas were found on all samples exposed in SP 3 with exception of the highest alloyed grades. A summary of corrosion performance for samples exposed in swimming pool halls is given in Table 7.

No significant case of stress corrosion cracking was detected after 72 weeks of exposure in three swimming pool halls. The worse conditions for corrosion of stainless steel samples was in SP 3. Only grades EN 1.4547 and 1.4410 were free of corrosion.

Corrosion on U-bend stainless steel samples after laboratory tests

Exposure of stainless steel with spots of chloride deposits at 50°C:

Stress corrosion cracks were found on all specimens of grade EN 1.4301 and samples exposed for 22 weeks were cracked completely. Similar observations were made for more alloyed grade EN 1.4404, but the extent of SCC was lower. SCC of EN 1.4404 probably initiated from pits. In Figure 1, shows that the cracks were branched and transgranular as typical for SCC of stainless steels in chloride environments. Super austenitic grades EN 1.4539 and EN 1.4547 showed no SCC. However, the extent of pitting corrosion increased with time of exposure. No significant difference was seen in the performance of the two grades EN 1.4539 and EN 1.4547. Specimens of duplex EN 1.4162 were pitted after exposure. The pitting density was usually high and in some cases all surfaces were covered with pits. The pits were small and often elongated. The results of the metallographic examination did not confirm the presence of cracks and only shallow pits were identified. The duplex grades EN 1.4362, EN 1.4462, and EN 1.4410 were all corroded in a similar manner. All samples had shallow etched areas on the surface see Figure 2. However, the corrosion was deeper in some places and it rather had a character of pitting. The corrosion morphology was somewhat different for the materials. It was purely selective in case of EN 1.4362 and 1.4462 and pitting combined with partly selective dissolution of one phase for EN 1.4410. Using scanning electron microscope (SEM) with EDS analyzer, the corroded phase was in all cases identified as the ferritic phase. This phase appears darker in the images.



Figure 1. N 1.4404, MgCl_2, 30 %RH, 22 weeks, (width 440 $\mu m.$



Figure 2. EN 1.4462, MgCl_2, 30 % RH, 22 weeks, (width 800 $\mu m)$

Exposure at 40°C and at 30 %RH:

SCC occurred on 1.4301 after 10 weeks of exposure with spots of magnesium chloride and the cracks were observed in two spots out of six. Pitting corrosion was observed as well. EN 1.4404 was pitted after 10 weeks under the same conditions. Stainless steels EN 1.4539 and 1.4547 were free of corrosion after 4 weeks but several small pits developed on the former grade after 10 weeks. Duplex grade EN 1.4162 was pitted after 4 weeks. After 10 weeks, the attack was more profound and it had more a form of etching. Samples of EN 1.4362 were only superficially etched. High-alloyed duplex materials EN 1.4462 and 1.4410 were slightly etched after 10 weeks. Austenitic EN 1.4301 and 1.4404 exposed with spots of calcium chloride showed cracks in all six contaminated zones after 10 weeks. EN 1.4301 was cracked through the whole profile. Grades EN 1.4539 and 1.4547 were pitted. Etched areas were found on the surface of duplex grades EN 1.4162, 1.4362, and 1.4462. The etching was apparently strongest for EN 1.4162. EN 1.4410 was less etched and the attack was closer to pitting. Samples exposed with spots of NaCl were completely free of corrosion. Slight discoloration was observed on samples of EN 1.4301 and 1.4462. Sodium chloride deposits were dry at the end of exposure.

Exposure at 30°C and at 30 % RH:

Small pits and tiny cracks originating from pits were found on austenitic grade EN 1.4301 under spots of magnesium chloride. Stainless steel grades EN 1.4404 and 1.4547 were pitted. Duplex materials EN 1.4162 and 1.4462 were etched. Very superficial etching was observed on EN 1.4410. Many small cracks often passing through pits in all spots of calcium chloride were seen on EN 1.4301. Even smaller cracks starting from small pits developed on steel grade EN 1.4404. Pitting was observed on EN 1.4547. The duplex grades EN 1.4162, EN 1.4462 and EN 1.4410 were etched and suffered from selective attacks.

Exposure at 20°C and at 30 % RH:

All materials contaminated with $MgCl_2$ were pitted. The only exception was duplex stainless steel grade EN 1.4162. for which, the appearance of the deterioration was closer to etching. The pitting density decreased from EN 1.4301 to EN 1.4547 and only few pits developed on duplex stainless steel grades EN 1.4462 and 1.4410. The appearance of stainless steels exposed with CaCl₂ spots was similar as to the results in $MgCl_2$. Some etched areas were noted on EN 1.4162. No stress corrosion cracking occurred at 20°C on any of the steel grades.

Discussion and summary

Results of all experiments are summarized in Table 8.

| Exposure conditions | Stainless s | steel grade, I | EN | | | | | |
|----------------------------------|-------------|----------------|---------|-------------|-------------|-------------|-------------|-------------|
| | 1.4301 | 1.4404 | 1.4539 | 1.4547 | 1.4162 | 1.4362 | 1.4462 | 1.4410 |
| 50°C, 30% RH, MgCl ₂ | SCC 6 | SCC 6 | Pitting | Pitting | Pitting | Pitting | Pitting | Pitting |
| 50°C, 17 % RH, CaCl ₂ | SCC 6 | SCC 6 | Pitting | Pitting | Pitting | 0.C. | Pitting | Pitting |
| 40°C, 30 % RH, MgCl ₂ | SCC 2 | Pitting | Pitting | <i>n.c.</i> | <i>O.C.</i> | <i>O.C.</i> | <i>O.C.</i> | <i>n.c.</i> |
| 40°C, 30 % RH, CaCl ₂ | SCC 6 | SCC 6 | Pitting | Pitting | <i>O.C.</i> | <i>O.C.</i> | <i>O.C.</i> | Pitting+ |
| 40°C, 30 % RH, NaCl | n.c. | <i>n.c.</i> | n.c. | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> | <i>n.c.</i> |
| 30°C, 30 % RH, MgCl ₂ | SCC 2 | Pitting | × | Pitting | <i>O.C.</i> | × | <i>O.C.</i> | <i>O.C.</i> |
| 30°C, 30 % RH, CaCl ₂ | SCC 6 | SCC 6 | × | Pitting | <i>O.C.</i> | × | Pitting | <i>O.C.</i> |
| 20°C, 30 % RH, MgCl ₂ | Pitting | Pitting | Pitting | Pitting | <i>O.C.</i> | Pitting | Pitting | Pitting |
| 20°C, 30 % RH, CaCl ₂ | Pitting | Pitting | Pitting | Pitting | <i>O.C.</i> | Pitting | Pitting | Pitting |

Table 8. Summary of **c**orrosion attack on U-bend samples exposed with deposits at different exposure conditions; SCC (with a number of zones with cracks)

Notes: + Tiny cracks; \times Not tested, O.C. Other corrosion forms, n.c. = No corrosion

It was indeed revealed that standard stainless steel grades 1.4301, 1.4401 and similar grades are not suitable in load bearing constructions at locations that are not possible to clean in swimming pool atmospheric environments, for example at the ceilings due to the high aggressiveness of these environments. The pH was low in the deposits and the probable cause is decomposition of chloramines, which leads to acidification. In the laboratory measurements the pH was not altered on the surfaces but SCC occurred anyway in temperatures above 20°C on the stainless steel grades of type 1.4301 and 1.4401. However, most corrosion found on the surfaces was of localized type and due to the mechanism for localized corrosion the pH is generally lowered in the pits in propagation of pitting corrosion. The transport of chlorides to the ceilings and the decrease in pH is most probably due to the chemical reactions of disinfection chemicals as sodium hypochlorite and the formation of chloramines. However, aerosols as transportation cannot be ruled out. The cyclic character of the relative humidity changes during daytime is due to changes in temperature, swimming activity, and switching off the air conditioning system overnight. These cyclic changes can cause condensation and also a situation where the relative humidity pass through the critical deliquescence points for the chloride salts of calcium and magnesium and cause the most critical corrosive environment.

There are recommendations in the European standard norm "prEN1993-1-4" that austenitic steels are suitable for many applications in indoor and outdoor swimming pools. For load-bearing members in atmospheres containing chlorides that cannot be cleaned regularly (e.g. in suspended ceilings above swimming pools) the following grades should be used: Pool water containing ≤ 250 mg/L chloride ions: 1.4539, 1.4529, 1.4547, 1.4565. Pool water containing ≥ 250 mg/l: 1.4529, 1.4547 (254 SMO), and 1.4565. This investigation confirms the previous recommendations and that 1.4547 (254SMO) showed the best performance and resistance to stress corrosion cracking compared to the other tested stainless steels. It should also be pointed out that this kind of SCC does not occur unless there are very specific criteria fulfilled in the environment as, deposits of chloride salts and very specific relative humidity for these salts in combination with temperature.

Conclusions

- Austenitic stainless steel grades similar to EN 1.4301 (S30400) and 1.4404 (S31600) should be excluded as a material for use in load bearing constructions in swimming pool atmospheric environments due to their susceptibility to SCC.
- Duplex stainless steels were typically etched or suffered from pitting corrosion rather than SCC.
- Due to the complexity in the assessment of the application limits for tested duplex stainless steels, based on the laboratory tests in this work, their application for load bearing constructions in swimming pool atmospheric environments cannot be recommended at present time. The tendency of austenitic stainless steels to SCC and pitting decreased with increasing PRE.
- Super austenitic stainless steels EN 1.4539 and 1.4547 showed no tendency to SCC.
- SCC did not occur below 20°C on any of the tested stainless steel grades in the laboratory measurements.
- Regular cleaning as and inspection of safety bearing components in stainless steels should be performed in swimming pool atmospheric environment.

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TRIBOCORROSION OF STAINLESS STEEL IN ACID SOLUTIONS: EFFECT OF LATENCY TIME AND CONTACT AREA

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Abstract

Tribocorrosion is the interplay between chemical, electrochemical, and mechanical processes leading to a degradation of materials in sliding contacts immersed in a corrosive environment. The tribocorrosion of stainless steel in a sulfuric acid aqueous solution is reported in this study. Electrochemical measurements performed during continuous and intermittent unidirectional sliding tests were used to monitor and to evaluate the chemical-mechanical degradation of that passivating material resulting from the periodic electrochemical growth and mechanical removal of passive surface films. The effect of latency time, which is the time in-between two successive contact events, on the wear volume and coefficient of friction is reported. Furthermore, the effect of hertzian contact area on the corrosion-wear of stainless steel is reported. Both parameters are common in industrial sliding mechanical parts.

Introduction

Tribocorrosion results in the degradation (wear, cracking, corrosion) of material surfaces subjected to the combined action of a mechanical loading (friction, abrasion, erosion), and a corrosive loading by the environment (chemical and/or electrochemical interactions). Such damage to mechanical parts due to corrosion and wear has a significant impact on the economics of engineering systems in terms of material loss and associated equipment downtime. The specific character of tribocorrosion is linked to the synergy resulting from the coupling of mechanical and environmental effects. The challenge for researchers and engineers is actually to find out how to turn over a negative synergism into a positive antagonism. Examples are self-lubricating and/or self-healing material surfaces. Industrial fields where tribocorrosion has already been identified are e.g. marine and off-shore equipment, hot strip mills, biomaterials used for orthopedic implants and hip and knee prostheses, cutting tools, chemical pumps, food processing and mining equipment, and nuclear reactor components like rod cluster control assembly and control rod drive mechanisms.

The in-depth analysis of the mechanisms behind tribocorrosion was recently initiated in different fields to clarify the in-situ durability of interacting material surfaces. That requires a multidisciplinary approach on material science, electrochemistry, tribology, mechanics, and surface science. The tribocorrosion behavior of sliding contacts depends on the mechanical solicitations that are related to equipment design and operation, the electrochemical conditions prevailing at the rubbing metal surfaces, the solution properties in the tribo-contact, and the materials and surface properties of the contacting bodies. These parameters usually do not act independently, but their effects on the tribocorrosion behavior are mutually interdependent. For instance, the interplay between chemical, electrochemical, and mechanical reactivity of Stellite and stainless steel surfaces was reported recently by Celis *et al.* [1], local mechanical and electrochemical behavior of duplex stainless steel was discussed by Vignal *et al.* [2], while the modeling of sliding wear from dry to wet environments was investigated by Jiang and Stack [3].

In this work, the effect of latency time and contact area on friction and wear behavior of stainless steel AISI 316 sliding against an inert counter-body immersed in an acid solution, is presented.

Experimental

AISI 316 stainless steel cylindrical samples with a diameter of 25 mm and a height of about 20 mm were immersed in 0.5 M H_2SO_4 kept at room temperature. The samples were prepared by polishing with 1 μ m diamond paste followed by an ultrasonic cleaning in acetone and successively in ethanol for 5 min. The flat circular top part of the cylinder with an area of 4.91 cm² was exposed to the electrolyte.

A unidirectional tribometer (Multispecimen-tester, Falex Tribology N.V., Belgium) was used with zirconia pin counter-bodies (radius 100 mm). A static normal force of 5 and 40 N was applied corresponding to a maximum hertzian contact pressure of 140 and 281 MPa respectively. A unidirectional tribometer (MUST-tester, Falex Tribology N.V., Belgium) was operated with corundum balls with a radius of 5 mm as counter-bodies at a low normal force of 0.1 N. That force corresponds to a maximum hertzian contact pressure of 281 MPa. The rotation rate was set at 120 rpm. The ball axis was positioned at 5 mm from the axis of the rotating cylinder. The test duration was 2,700 or 5,000 cycles. Continuous and intermittent sliding tests were performed. During continuous sliding tests, the counter-body rotated permanently during the whole duration of the tests. The latency time, t_{lat} , is then equal to the rotation period, T_r , namely 0.5 sec. On the contrary during intermittent sliding tests, the pin was successively rotated for one cycle and then kept immobile for a certain period of time. This sequence was repeated till the total test duration was reached. The latency time in such intermittent experiments is equal to $t_{lat} = T_r + t_{off}$, and was selected at 5 and 50 sec. A bidirectional tribometer (MUST-tester, Falex Tribology N.V., Belgium) operated with polished corundum balls as counter-bodies (radius 5 mm), was used to measure the coefficient of friction. In this tester, the counter-body was glued on a cantilever with the following elastic constants: $K_t = 2.444$, $K_n = 0.978$. A stroke length of 0.5 mm, a maximum sliding speed of 1 mm/s, and a normal force of 0.1 N for 1,000 cycles were used.

In all sliding tests, a platinized titanium gauze was used as counter-electrode and a saturated sulfate electrode (SSE) as reference electrode for open circuit potential, E_{oc} , measurements. After the tests, the samples were removed from the electrolyte, rinsed with de-ionized water, and dried in warm air. The volumetric material loss in the wear tracks was measured by white light profilometry (Micromesure, STIL, France). The surface microstructure was identified by scanning electron microscopy (Philips FEG 30 SEM).

Results

Open circuit potential evolution

In the study of tribocorrosion, the variation of open circuit potential of the test sample (Figure 1) allows an evaluation of the surface state of that material. Upon immersion in the electrolyte, the E_{oc} of freshly polished stainless steel is low indicating the presence of an active surface state (period 1 in Figure 1). After some time of immersion in aerated solutions, spontaneous electrochemical surface reactions lead to the formation of a stable passive surface film, consisting mainly of chromium oxide. The formation of that passive surface film causes the rise of the open circuit potential (period 2 in Figure 1). At the time sliding is activated, the open circuit potential drops to a value corresponding to the one of the initial active state. This

indicates that the passive film is removed by the mechanical interaction. Part of the wear track becomes active [4], and a galvanic couple is established between worn and unworn areas at the sample due to their different open circuit potentials (period 3 in Figure 1). At the time that sliding is interrupted or ended, the wear track progressively repassivates, and the increase of the open circuit potential indicates the re-growth of a passive surface film (period 4 in Figure 1).



Figure 1. Evolution of the open circuit potential with immersion time of stainless steel in 0.5 M sulfuric acid before (periods 1 and 2), during (period 3), and after (period 4) continuous unidirectional sliding at a normal force of 5 N.

The evolution of the open circuit potential during continuous sliding was recorded under test conditions where two different contact areas were achieved on stainless steel immersed in a sulfuric acid aqueous solution, (Figure 2). Hereto the counter-body radii and the normal loads were varied so that an identical maximum contact pressure of 281 MPa was achieved in both cases but with hertzian contact areas of 0.0005 mm² and 0.2137 mm² respectively. The increased potential drop noticed reveals that the larger contact area results in a larger depassivated area. The fact that an identical contact pressure was achieved in both tests assures that the difference in open circuit potential noticed is caused only due to a varying ratio of active-to-passive area, and not to any mechanical effect (e.g. elasto-plastic deformation, induced phase transformation). The difference in wear track area size is clearly appearing from the SEM micrographs of the wear tracks after the sliding tests shown in Figure 3.



Figure 2. Evolution of the open circuit potential of stainless steel AISI316 immersed in 0.5 M sulfuric acid during (a) start up, and (b) final stage of continuous unidirectional sliding against zirconia performed under hertzian contact areas of either 0.0005 or 0.2137 mm^2 .



Figure 3. Scanning electron micrographs of stainless steel after continuous unidirectional sliding against zirconia in 0.5 M sulfuric acid performed for 2,700 cycles under hertzian contact areas of (a) 0.2137 mm², and (b) 0.005 mm².

A zoom-in on the variation of the open circuit potential in period 3 (cf. Figure 1) recorded during continuous and intermittent unidirectional sliding tests performed at different latency times is shown in Figure 4. During continuous sliding tests at a latency time of 0.5 s, the open circuit potential is stable around -0.82 V vs. SSE. This potential is a mixed potential resulting from a dynamic equilibrium between active and passive areas inside and outside the wear track obtained under a constant rotation rate of the counter-body. During intermittent sliding tests performed at a latency time of 5 sec, the open circuit potential drops during sliding periods and rises during non-sliding periods, resulting in a fluctuation of the open circuit potential between -0.82 and -0.74 V vs. SSE. The drop of the open circuit potential reveals the removal of the passive layer. The progressive increase of E_{oc} during the period that the counter-body is immobile indicates the progressive re-growth of the passive film. At a latency time of 5 s, a dynamic equilibrium is not achieved since no potential plateau value is reached. A similar trend is noticed at a latency time of 50 sec but with open circuit potential fluctuations that are more pronounced, namely between -0.73 and -0.59 V vs. SSE. At increasing latency time, more time is thus given to the passive film to re-grow during non-sliding periods, and therefore the effect of the passive film thickness on the tribocorrosion of stainless steel is decoupled from the sliding speed.



Figure 4. Open circuit potential evolution during continuous and intermittent unidirectional sliding of stainless steel AISI 316 against zirconia balls in 0.5 M sulfuric acid at a normal force of 5 N.

Wear volume and friction coefficient

After the sliding tests, the wear track volume was measured (Figure 5). A dependence of the material loss on the experimental parameters is appearing. The wear volume increases markedly at increasing latency time. This indicates that when the passive film is thicker, a larger amount of

material is removed from the sample in contact with the counter-body. Additional electrochemical impedance spectroscopy measurements can be done during sliding to measure the corrosion of the active and passive areas of the sample surface. Such tests are a possible methodology that allows decoupling the mechanical and electrochemical contributions of the different areas of the sample surface. That has been shown to lead to an identification of the material degradation processes in the tribocontact as well as an explanation of the synergistic effects in tribocorrosion processes [5]. Furthermore, it was shown that an increased contact area has a detrimental effect on the tribocorrosion resistance of sliding materials.



Figure 5. Effect of latency time (2700 cycles) and contact area (5000 cycles) on the wear volume on stainless steel after unidirectional sliding tests against zirconia balls in 0.5 M sulfuric acid.

The evolution of the coefficient of friction with latency time is shown in Figure 6. It is noticed that after a running-in period, a coefficient of friction around 0.7 is measured at the different latency times. The running-in period decreases at increasing latency time indicating a dependence of the coefficient of friction on the latency time at short sliding durations.



Figure 6. Evolution of the coefficient of friction recorded during continuous and intermittent unidirectional sliding tests on stainless steel AISI316 against zirconia balls immersed in 0.5 M sulfuric acid.

Conclusions

The corrosion-wear of AISI 316 stainless steel was investigated by performing unidirectional continuous and intermittent sliding tests against zirconia balls immersed in a sulfuric acid aqueous solution. The evolution of the open circuit potential was used to monitor the passive/active surface state of the stainless steel sample indicating the removal or re-growth of the passive surface film. A change of the latency time during sliding tests allows modifying the thickness of the passive film in between successive contact events. Both the amount of material loss and the evolution of the coefficient of friction depend on the thickness of that passive film indicating that there is a strong interaction of the tribocorrosion process on the surface characteristics in the tribocontact. Sliding tests done at the same contact pressure but at different hertzian contact areas allowed to decouple mechanical from geometrical effects. Such an investigation done on the tribocorrosion behavior of stainless steel, revealed a dependence of the wear volume on the hertzian contact area. The different active-to-passive area ratios achieved in that way are reflected in the evolution of the open circuit potential.

This research demonstrates that an in-depth analysis of the different chemical, mechanical and electrochemical contributions to material loss during tribocorrosion may lead to a better selection of materials for use under tribocorrosion field conditions. A protocol for the evaluation of the tribocorrosion synergism of common and novel materials is hereto a must [5].

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ULTRASONIC TESTING OF CLAD PLATES FOR EVALUATION OF HYDROGEN DEGRADATION

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Abstract

In this paper, results from ultrasonic investigation on hydrogen degradation in clad plates processed by the explosive method are presented. The clad plates studied were made of carbon or low alloy steel plates with a thin layer of stainless steel (ferritic or austenitic). The specimens were thermocycled for 30 and 100 times in the temperature range of 25-450°C in hydrogen gas atmosphere with fast cooling rates. These parameters simulate the operating conditions of industrial installations. The results of ultrasonic investigations were verified by light microscopy on cross sections of specimens. It was found that nondestructive ultrasonic investigation allows to estimate the level of hydrogen degradation in clad plates from hydrogen interactions.

Introduction

Structural elements of industrial installations are made of clad plates, which are particularly endangered to hydrogen degradation. The hydrogen degradation process is known to occur especially in the places, where installation shut downs can occur from high temperatures, which results in significant temperature gradients. Additional impact from hydrogen degradation is a strong accumulation of microstructure defects created in the process of explosive joining. Due to the presence of discontinuities such as voids, which can be traps for hydrogen, the underclad cracking and destruction of the material may occur. For this reason, the preparation of the joints, material purity, differences in the hydrogen diffusion rate and solubility in clad and parent material as well as differences in microstructure are parameters of paramount importance [1,2]. Furthermore, hydrogen degradation of clad plates appears most frequently as underclad cracking [3], which leads to delamination and splitting of clad from the parent plate. This calls for development of methods for monitoring degradation elements, which can be exposed to assess the hydrogen degradation. In industrial installations, in this context nondestructive tests are of paramount importance. In this paper, a method based on ultrasonic investigations has been used for NDT evaluation of hydrogen degradation in clad plates.

Experimental

Test material

Specimens made of carbon steel A516 grade 60 cladded with the ferritic stainless steel 410 S (specimen no. 1) and of low-alloy steel 13CrMo4-5 cladded with the corrosion resistant austenitic steel 304 L (specimen no. 2) were tested ultrasonically and also using metallographic procedures. The chemical compositions of the examined plates are given in Table 1. Dimensions of the specimens were 160 x 25 x 10 mm with the thickness of flyer plate equal to 3 mm. The specimens were investigated before and after thermal cycling in hydrogen environment; with 30 and 100 thermal cycles (30T and 100T). The parameters of thermal cyclic process were

reflecting in-service conditions, sudden stoppages and start-ups, in a laboratory environment. Each cycle consisted of:

- heating to 450°C followed by annealing for 30 minutes in hydrogen gas (under hydrogen pressure of 0.15 0.3 MPa),
- fast cooling to room temperature followed by 30 minutes holding.

The heat was removed from the ends of specimen.

| | | с | Si | Mn | S | Р | Cr | Ni | Мо | N | Cu |
|--------|-------------|-----------|-----------|-----------|--------------|--------------|-----------|----------|-----------|-------------|------|
| Specim | iens no. 1 | max 0,21 | 0,15-0,40 | 0,60-0,90 | max | max | - | - | - | - | - |
| Parent | A516 Gr. 60 | | | | 0,035 | 0,035 | | | | | |
| Flyer | 410S | max 0,08 | max 1,00 | max 1,00 | max 0,030 | max 0,040 | 11,5-13,5 | max 0,60 | - | - | - |
| Specim | iens no. 2 | 0,08-0,18 | max 0,35 | 0,40-1,00 | max | max | 0,70-1,15 | - | 0,40-0,60 | max | max |
| Parent | 13CrMo4-5 | | | | 0,010 | 0,020 | | | | 0,012 | 0,00 |
| Flyer | 304L | max 0,03 | max 0,75 | max 2,00 | max 0,030 | max 0,045 | 18,0-20,0 | 8,0-12,0 | - | max 0,10 | - |

Table 1. The chemical compositions of specimens examined according to standards specifications

Ultrasonic flaw detection

Ultrasonic tests were carried out with a Panametrics flaw detector Epoch 4, using the echo method [4] according to ASTM A 578 "Standard Specification for Straight-Beam Ultrasonic Examination of Plain and Clad Steel Plates for Special Applications". The measurement frequency was 20 MHz and the transducer probe of 3 mm size was used for small discontinuities. The frequency higher than the standard frequency was used to detect fine changes in specimens, especially in the flyer-parent joint area.

Microstructural metallographic examination

Cross sections of the flyer-parent joint were examined with a metallographic light microscope (LM) and a scanning electron microscope (SEM). On the basis of the results of ultrasonic tests, areas, which indicated the presence of some discontinuities, were selected for detailed microstructural examinations. Specimens for observations were cross-sectioned in specific locations, ground using abrasive papers, mechanically polished with diamond pastes and chemically etched with 4% Nital.



Figure 1. Example of areas showing discontinuity indications in ultrasonic studies

Results

Ultrasonic flaw detection

The equipment used for flaw detection allows to detect imperfections in the bonding interface.

The discontinuities at the interfaces were found based on the changes of in the amplitude signals. Examples of ultrasonic wave spectra for the examined specimens are shown in Figures 2-4. In accordance to ASTM A578 standard acceptable intensity of the peak derived from flyer-parent joint must not exceed 50% of the peak intensity derived from the specimen. This value was exceeded in none of the specimens, in spite of employing frequency higher than the standard. Hence, the results of ultrasonic testing proved a high quality of flyer-parent joints in the present study.



Figure 2. Ultrasonic wave spectra of specimens - initial state; a) specimen no. 1, b) specimen no. 2



Figure 3. Ultrasonic waves spectra of specimens after 30T; a) specimen no.1, b) specimen no. 2



Figure 4. Ultrasonic wave spectra of specimens after 100T; a) specimen no. 1, b) specimen no. 2

The signals derived from certain areas with a high echo intensity were also observed (Figures 2-4). A significant increase in the signal amplitude, reflected from the bonding interface, with the increase of the number of thermal cycles, was detected. This suggests the increase of discontinuities with the increase of trapped hydrogen.

Microstructural metallographic examination

In order to reveal the geometry of discontinuities found by ultrasonic testing, metallographic examinations were carried out in specific locations. Images of the microstructures revealed in

these locations are given in Figures. 5-6. Metallographic examinations on the cross sections of clad plates showed that the bonding interface has a typical wavy morphology [5], with local melted zones.



Figure 5. Microstructure of specimen no. 1: (a) - initial state; (b, c) - after 30T; (d, e, f) - after 100T



Figure 6. Microstructure of specimen no. 2: (a, b, c) – after 30T; (d, e, f) – after 100T; (f) – after 100T, SEM image

Microscopic examinations carried out on the samples subjected to 30 thermal cycles in hydrogen revealed no changes in the microstructure. The numerous micro-pores shown in Figure 5a were present already prior to hydrogen thermo-cycling and being typical of the explosive bonding. Microstructure of the sample series 1, exposed to 100 thermal cycles in hydrogen, despite a clear increase of the ultrasonic signal from the joint, looks similar to the one subjected to 30 cycles. In the case of the sample series 2, after 30 hydrogen thermal cycles, examinations of the areas using a higher amplitude of ultrasonic signal only revealed micro-pores, as already explained, also appearing in as-bonded material (Figures 6a, b, c).

On the other hand, in the samples treated with 100 thermal cycles, micro-cracks have been

created at the interface between the bonded plates (Figures 6d, e, and f). The results of the investigations show that an increase in the ultrasonic amplitude detected can be a result from either hydrogen trapping in the pre-existing pores or hydrogen induced microcracking along the bonding interface.

Summary

Ultrasonic examinations of the bonding in the clad plates are usually carried out employing waves with the frequency in the range of 2-5 MHz. In the present study, the 20 MHz frequency was used. Such an increased frequency permits the detection of fine imperfections such as micro-cracks and micro-pores with trapped hydrogen.

The results of these investigations demonstrate that the described procedure of ultrasonic examinations can be employed in an industrial environment for detection of subtle flaws caused by hydrogen degradation. This in turn helps to prevent possible delamination of clad plates.

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A TOOL AND METHODS FOR PREDICTING PITTING CORROSION RISK OF STAINLESS STEELS IN EVAPORATED CONDITIONS

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Abstract

The corrosion resistance of stainless steels is usually good, thus they are extensively used as construction materials in various environments. In some cases, however, localized corrosion has caused unexpected material failures in environments considered safe. The risk may become high and a basically harmless environment can change dramatically if there is a possibility of concentration due to evaporation of water. Some salts may start to precipitate and thus the ionic ratios of solution in contact with stainless steel can change in to the direction favoring corrosion. In this study experiments in chloride and chloride-sulfate solutions with different concentrations were performed with austenitic stainless steels EN 1.4301 and EN 1.4432 as well as with one duplex stainless steel EN 1.4462 with temperatures up to 70°C. To be able to consider the effect of evaporation, changes due to precipitation of different compounds were modeled. An excel-based tool was developed for evaluation of pitting corrosion risk of different types of stainless steel in various environments where the concentration of solution is possible.

Introduction

Due to the good corrosion resistance, stainless steels are nowadays increasingly used as construction material in diverse environments and applications. Uniform corrosion is not a concern in most cases. However, in environments containing chlorides, there is a risk for localized corrosion of stainless steels. In some cases, pitting corrosion or stress corrosion cracking have caused unexpected failures in environments chemically considered harmless. This risk increases if there is a possibility of evaporation of water producing to the concentration of the solution. It is generally known that the susceptibility of localized corrosion increases with increasing chloride concentration and decreases with increasing sulfate to chloride ionic ratio¹. Precipitation of sulfur compounds can drastically change this ionic relationship². Sodium and calcium are the most common cations in natural waters. The solubility of calcium sulfate in water is clearly smaller than that of sodium sulfate. Thus the water containing calcium, sulfate and chloride can change to almost pure chloride solution if the concentration of calcium is high enough to be able to precipitate all or most of the sulfate. In these cases the concentration of sulfate in the beginning could have been multifold compared to that of chloride. The corrosion failures of splash zones of paper machines as well as the catastrophic stress corrosion cracking failures of stainless steel swimming pool roof constructions are examples of evaporation caused phenomenon^{3,4}.

The aim of these studies was to develop procedures and methods to verify the localized corrosion risk of stainless steels in applications where the concentration of the solution due to evaporation is possible. Based on the experimental data, a pitting corrosion susceptibility database of the studied stainless steels was created. A quantitative corrosion risk prediction and a quantitative

pitting corrosion model considering the relationships between different variables were developed. Based on these empirical models a MS Excel tool was developed to predict the pitting corrosion risk of stainless steels in applications where concentration of the water due to evaporation is possible.

Experimental

The test materials used in this study were two austenitic stainless steels EN 1.4301 and EN 1.4432, and one duplex stainless steel EN 1.4462 manufactured by Outokumpu Stainless, Table 1. One ferritic grade (EN 1.4003) manufactured by Rautaruukki was also investigated, but these results are presented elsewhere⁵. All experiments were performed in as received state; grades EN 1.4301 and EN 1.4432 received in 2B condition (cold-rolled, heat-treated, pickled and skin-passed, surface finish 2B) and grade EN 1.4462 was received as imeas-brushed condition. Prior to experiments the surfaces were cleaned with acetone, rinsed with water and ethanol and air-dried.

| Material | С | Si | Mn | Р | S | Cr | Ni | Мо | Cu |
|-----------|-------|------|------|-------|-------|------|------|------|------|
| EN 1.4301 | 0.049 | 0.50 | 1.59 | 0.038 | 0.002 | 18.2 | 8.1 | 0.18 | 0.40 |
| EN 1.4432 | 0.019 | 0.47 | 1.69 | 0.034 | 0.004 | 16.5 | 10.6 | 2.56 | 0.45 |
| EN 1.4462 | 0.024 | 0.35 | 1.52 | 0.027 | 0.002 | 22.5 | 5.7 | 3.2 | 0.16 |

Table 1. The main components (%, w/w) of studied stainless steels

The pitting susceptibility of the test materials were evaluated with potentiodynamic polarization measurements. The experiments were made using a special test cells allowing simulation of stagnant conditions, avoiding crevice corrosion and eliminating the effect of convection^{2,4-6}. The test solutions were made of distilled water and reagent grade sodium chloride (NaCl) and sodium sulfate (Na₂SO₄). The chloride content varied from 0.002 mol/l (0.071 g/l Cl⁻) to 5 mol/l (177.5 g/l Cl⁻). The concentration of sulfate varied from 0 to 1 mol/l (0... 96 g/l SO₄²⁻), the smallest amount added being 0.01 mol/l (0.96 g/l SO₄²⁻). When sulfate was used, the molar ratio of sulfate to chloride varied between 0.01 and 2. Temperatures up to 50 °C were used for the austenitic stainless steels EN 1.4301 and EN 1.4432. For the duplex stainless steel EN 1.4462 tests were performed only at elevated temperatures ranging from 40 to 70°C.

Before starting cyclic anodic polarization, the open circuit potential (E_{oc}) was monitored for 15 to 30 minutes. An Ag/AgCl electrode was used as a reference electrode and platinum wire as a counter electrode. The polarization was started from open circuit potential with a scan rate of 0.1 mV/s. The polarization was reversed when the current achieved the value of 200 μ A (current density ~ 30...45 μ A/cm²). The scan rate for reversed curve was 0.5 mV/s. A critical pitting potential was defined from the curves to be the potential, where the value of current suddenly and permanently grows. After the experiments the specimens were inspected visually and by a low magnification optical microscope to verify the form of possible corrosion.

Since water chemistry modeling tool developed is based on solubility product values ignoring activity coefficients, soluble complex compounds, and crystallization of various polymorphs including different crystal water amounts, a comparative study with computer programs MIN-EQL+ Version 4.5 and OLI Systems Inc Lab Analyzer and Stream Analyzer 3.1 was performed. These programs evaluate chemical equilibrium taking into account items mentioned above. Approaches of these programs were different and considerable qualitative and quantitative distinctions between databases were evident. Also, dealing with thermodynamic calculations in general, it must be noticed that kinetics are ignored. An essential feature of the calculations, the targeted systems was described with four equilibrium equation types: 1) ligand protonation, 2) metal

complex formation, 3) metal hydrolysis and 4) ionic product of water. The results of ion-product model and calcucations of MINEQL were compared to each other.

Results and discussion

Results of the polarization measurements have been reported in more detail earlier^{2,4,5,6}, thus this paper concentrates on the developing of the tool for predicting pitting corrosion risk. Critical pitting potentials (E_p) were determined from each polarization curve and these potentials were used as a database for the modeling.

Modeling of the critical pitting potential

The dependence of the pitting potential on the chloride concentration in a plain chloride solution can be approximated by an equation of the form

$$E_{p} = A - k \cdot \log([C\Gamma]), \qquad (1)$$

where E_p is the pitting potential (mV), [Cl⁻] is the chloride concentration (mol/l), and A and k are parameters dependent on the temperature and the sulfate concentration.

It is reasonable to expect that at very low chloride concentrations no pitting will take place at any potential. Also, the measurement data indicate that at high chloride concentrations the dependency deviate from the form of Equation (1) to lower values. These effects can be taken into account by adding two terms to Equation (1):

$$E_{p} = A - k \cdot \log([Cl^{-}]) + D/([Cl^{-}])^{n} - B \cdot ([Cl^{-}])^{m},$$
(2)

where D, B, n and m are parameters dependent on the temperature and the sulfate concentration. The values of the parameters used in equations have been chosen so that all the data points lie on or above the corresponding curve and that the effect of temperature is reasonable and the difference at all chloride concentrations is logical. An example of this modeling is seen in Figure 1a. A more detailed description of the quantitative corrosion risk model approach for EN 1.4301 can be found from earlier papers^{2,4,5,6}. In this paper models have been further developed according to the specified new results and extended also to stainless steel grades 1.4432 and 1.4462.

Modeling of the salt precipitation

To be able to consider the effects of concentration, due to precipitation of certain salts, on pitting susceptibility, the changes in the composition have to be known. In this work a simplified method based on the use of ionic product of pure salt in saturated solution as a criterion for the precipitation to estimate the changes of the concentrations and ionic ratios of chloride and sulfate ions was used. The solubility of sodium chloride in water at the temperature of 25° C is about 5.4 mol/l (about 190 g/l Cl⁻) and that of sodium sulfate is 1.9 mol/l (182 g/l SO₄²⁻). At the temperature of 40° C the solubility's are correspondingly 5.5 mol/l (195 g/l Cl⁻) for sodium chloride and 3.0 mol/l (288 g/l SO₄²⁻) for sodium sulfate. In Figure 1b the borderlines for the solubility's of these salts at the temperature of 25 °C are shown. The "equation" marked in the figure shows the solubility limits for sodium sulfate according to following equation:

$$[SO_4^{2^-}] = 2.27 \cdot e^{-0.152} \cdot [CI^-] - C$$
(3)

The arrows in Figure 1b point the development of concentrations due to the evaporation in case where the molar concentrations of chloride and sulfate in the beginning are equal. In units of g/l the amount of sulfate is 2.7 times that of chloride. The precipitation of sulfate begins when the

concentrations are about 1.4 mol/l (150 g/l SO_4^{2-} and 50 g/l Cl⁻). After this the chloride content of the solution continues to increase while the sulfate content decreases if the evaporation still continues.



Figure 1. a) empirical model of pitting potentials of stainless steel EN 1.4301 in chloride-sulfate solutions b) Solubility limits for sodium sulfate and sodium chloride estimated by the ionic products of pure saturated salt solution.

If the solution contains besides sodium, chloride and sulfate, also calcium, the situation can change notably. The solubility of calcium sulfate is just a fraction of that of sodium sulfate (0.015 mol/l at 25°C). When this type of solution concentrates, it can be expected that practically all of the sulfate or calcium precipitates depending on which one is in lesser amount. In this case the effective sulfate content could be the value obtained by subtracting the amount of calcium: $[SO_4^{2^-}]_{eff} = [SO_4^{2^-}] - [Ca^{2^+}]$. This means that if the content of calcium in moles is as high as or higher than that of sulfate, all the sulfate precipitates from the solution already before the chloride concentration due to evaporation has even increased to high values⁵.

In the developed ion-product model, momentary ion products (without applying any activity coefficients) were compared with tabulated solubility products. In Figure 2. results provided by this model are compared with those by the MINEQL+. A significant correspondence between these two models prevails, indicating that the developed ion-product model can be applicable in practical cases. It is, however, strongly recommended that results of the ion-product model are regularly compared with results of simulation programs.



Figure 2. The concentrations of chloride and sulfate as a function of concentration rate calculated by ion-product model and by computer program Mineql+.

Pitting corrosion risk prediction

Based on the empirical models (Figure 1b) a MS Excel-based tool was developed for evaluation of pitting corrosion risk of stainless steels in evaporated conditions. In the tool the pitting corro-

sion risk prediction is based on the calculation of critical pitting potential (E_p). For the E_p calculation in-formation from the steel grade, temperature as well as chloride, sulfate and calcium contents is needed as input values. The effect of concentration on the chloride and sulfate content due to water evaporation is taken into account via concentration factor, which indicates how much the ionic strength is multiplied due to evaporation. In the second stage the calculated critical pitting potential (E_p) is compared to corrosion potential of the material. And if the corrosion potential is not known, the E_p is qualitatively compared to the oxidizing capacity of the environment, Table 2.

The pitting corrosion risk is given as integer number using linear scale from 0 to 100. The numerical value is dependent on the calculated critical pitting potential and oxidizing capacity as shown in Table 3. Finally the expected corrosion risk is presented both with numerical value and verbally, Table 4.

Table 2. Classification for the potential ranges.

| Potential range/ mV vs Ag/AgCl | Oxidizing capacity |
|--------------------------------|---|
| -3000 | very low, i.e. oxygen removed |
| -150150 | e.g. weaker oxidizers than dissolved oxygen present |
| 0300 | normal e.g. only dissolved oxygen present |
| 200550 | high e.g. hydrogen peroxide, dithionite, chlorite present |
| 550900 | extremely high e.g. chlorine, chlorine dioxide, ozone present |

Table 3. Pitting corrosion risk dependency from the calculated critical pitting potential and oxidizing capacity of the environment.

| Oxidizing capacity | Value 100 | Value 1000 | Value 0 |
|--------------------|------------------------------------|---|--------------------------|
| very low | $E_p < -300 \text{ mV}$ | $300 \text{ mV} < \text{E}_{\text{p}} < 0 \text{ mV}$ | $E_p > 0 mV$ |
| low | $E_{p}^{\prime} < -150 \text{ mV}$ | $-150 \text{ mV} < \dot{E}_{p} < 150 \text{ mV}$ | $E_{p} > 150 \text{ mV}$ |
| normal | $\dot{E_p} < 0 \text{ mV}$ | $0 \text{ mV} < \text{E}_{\text{p}} < 300 \text{ mV}$ | $E_{p} > 300 \text{ mV}$ |
| high | $E_{p} < 200 \text{ mV}$ | $200 \text{ mV} < E_p < 550 \text{ mV}$ | $E_{p} > 550 \text{ mV}$ |
| extremely high | $E_{p} < 500 \text{ mV}$ | $500 \text{ mV} < E_p < 900 \text{ mV}$ | $E_{p} > 900 \text{ mV}$ |

Table 4. Classification of pitting corrosion risk.

| Numerical value | Pitting corrosion risk |
|-----------------|------------------------|
| 0 | insignificant |
| 129 | minor |
| 3069 | moderate |
| 7099 | high |
| 100 | very high |

Examples of the pitting corrosion risk predictions given by the model for the grade 1.4432 are shown in the Figure3. Calcium has clearly detrimental effect on the pitting corrosion resistance in applications where concentration due to water evaporation is possible. Calcium reduces the amount of free sulfate via calcium sulfate precipitation.

Conclusions

The developed quantitative model approach can be used to predict pitting corrosion risk of stainless steels in chloride and chloride-sulfate solutions. The spreadsheet computational tool increases the usability of the experimental results and allows user to change input values and estimate the corrosion risk in various environments.

| EN 1.4432 Temperature range 1532 °C | | | | | | (Only chloride, sulphate, sodium and calcium are taken into consideration) | | | | | | | |
|--|---|---|--|------------------|-------|--|---|---|--|--|--|--|---|
| Initial information: | | | ret | urn / p | aluu | | Evalua | tion of | pitting c | orrosion | risk | | |
| Temperature, °C | (1532) | 23 | °C | 1 | | ۲ | | Critical | potential | 800 | mV | VS. : | sat. Ag/AgCI |
| Water composition | 1: | | | 1 | | | | r | | | | | |
| lon | | Conter | nt | 1 | | | 5 extrem | nely high | : | 25 | | | |
| Chloride, CI | (1 71 000) | 50 | mg/l | | | | iron | - | | | | | |
| Sulphate, SO42 | (0 96 000) | 25 | mg/l | 4 | | • | env | high |) | | | | |
| Calcium, Ca ²⁺ | (0 35 021) | 50 | mg/l | 4 | | ► | / of th | normal | , | | | | |
| | [SO4"]/[CI] = [Ca++]/[SO4"] = | 0,18 4,80 | | | | | ng capacit | low | , | | | | |
| Concentration fa | ictor | 1 | | 1 | | Þ | cidis li | very low | , | | | | |
| 1,000 dm³ rem | aining from initial 1 dm | n" | | | | _ | ô | · L | | | | | |
| Concentration | of the solution | n | | _ | | | | 0 | 20 | 40 Pitting corr | 60 osion risl | 80 | 100 |
| Concentrated so | lution | | | | | | | | | Thung bon | 051011115 | • | |
| | Chloride | 50 | mg/l | T | | | Pitting co | rrosion ris | k | Criteria of | the oxidi: | sing ca | pacity |
| | Sulphate | 25 | mg/l | | | | 0 | insignifi | ant | -300 . | 0 | mV | very low |
| | [\$04]/[01] = | 0,18 | | 1 | | | 3069 | minor modera | te | -150. | 150 | mv mV | iow normal |
| CaSO, prec | initatos whon concepts | ation factor | > 26.5 | Т | | | | high | | 200 . | 550 | mV | hiah |
| pico | ipitates when concentra | | | | | | 7099 | ngn | | | | | |
| Na ₂ SO ₄ prec | Temperature | ation factor | > 15439 | 32 °C | | | 100 (Only c | very hig hloride, st | h Jphate, sodi | 500 . um and cale | 900 :ium are | mV taken | extremely high |
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Figure 3. Effect of concentration on the pitting corrosion risk of EN 1.4432 in a) original solution and b) contrated by a factor of 500.

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THE AVESTA MULTICELL – A POWERFUL TOOL FOR RANKING PITTING RESISTANCE OF STAINLESS STEEL

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Abstract

The Avesta multicell has recently been introduced to compare the pitting resistance of multiple samples in one single measurement. In this study, the resistance to localized corrosion of a set of standard grades was compared with this method. Ranking experiments were performed by recording pitting potentials for six samples simultaneously and were found consistent with literature. The highest resistance was found for the ferritic grade 444 together with 304 and LDX 2101[®]. The localized corrosion resistance of the better 200 series grades compared well with high end ferritics such as 444.

Introduction

Laboratory experiments to estimate the corrosion resistance of stainless steels all have their limitations, but two main advantages: they are much cheaper and faster than on-site testing. Recent market trends have created renewed interest in alternatives to the standard austenitic grade 304L. For this reason, it is interesting to establish ranking tables for new variants of the classic 200-series alloys, as well as for new developments including the lean duplex grade LDX 2101[®]. This paper presents the Avesta multicell as a tool for ranking different steel grades.

The 200-series alloys are materials that have experienced renewed interest in recent years. They are high in manganese and nitrogen, and consequently sensitive to high sulfur levels. Modern metallurgical methods, however, give a consistent low sulfur content, thus modern variants offer a good corrosion resistance at a competitive price. Manganese is often added as an austenite former, but as Mn is a weaker austenite former than Ni, 2 wt% of Mn is needed to obtain the same effect as 1 wt% Ni. This decreases the maximum chromium content in the alloy, which means that 200-series grades have a lower corrosion resistance than the standard austenitic grades i.e. 304 [1, 2, 3]. The austenite formers, copper and nitrogen, are also frequently added to these alloys. Nitrogen has an effect on the mechanical properties, which results in the 200-series grades being generally stronger and harder than the 300-series. A more detailed survey of general properties of the 200-series has recently been published by Schwind et al. [4].

High-end alloy development of new steel grades often employs the ranking method ASTM G 150 standard for establishing critical pitting temperatures (CPT) [5]. For standard grades, this is not possible since the CPT will fall below the freezing point of the standard electrolyte. The pitting potentials for the different steel grades were measured using the Avesta Multicell, a novel design based on the single cell concept introduced some 20 years ago [6-7]. Pitting potential measurements normally require better statistics and thus a tool with higher throughput than the standard single cell. The multicell allows for simultaneous recording of pitting data from six samples. It can be used to measure pitting potentials as well as critical pitting temperatures by

using a single potentiostat, which will increase the laboratory throughput. This approach has previously been suggested by Shibata and Takeyama [8] already in the 1970s; their concept was then developed further by Baroux [9]. A crevice-free multicell was also reported by Jargelius-Pettersson et al [10]. The present solution was built using one standard potentiostat and additional standard electronics hardware and is thus very competitive in price compared to dedicated solutions. It also benefits from an improved temperature control compared to the setup used by Jargelius-Pettersson. For the interested reader, a thorough treatment of the literature is given in the monograph by Z. Szklarska-Smialowska [11].

Experimental procedure

Material

This study was designed to evaluate the performance of the multicell with particular focus on standard grades, including three manganese-containing grades from the 200-series, three ferritic grades and one lean duplex grade as well as the standard austenitic grade 304. Table 1 shows the chemical compositions. The ferritic grades 430, 439 and 444 are competitor materials whereas the austenitic grades 304, 201, 201Cu, 204Cu, the duplex grade LDX 2101[®] and the ferritic grade 430 (OK) were all manufactured by Outokumpu.

Samples of size 30×30 mm, allowing a test area of 1 cm², were wet ground to 320 mesh using SiC paper. The samples were rinsed in ethanol, dried in a clean air stream and left in laboratory atmosphere for at least 18 hrs prior to the measurements.

| Grade | EN | С | Si | Mn | Cr | Ni | Mo | Cu | Ν | Ti | Nb | S |
|-----------------------|--------|-------|------|------|------|-----|------|------|------|-------|-------|-------|
| 430 | 1.4016 | 0.043 | 0.27 | 0.32 | 16.0 | 0.2 | 0.01 | 0.01 | 0.04 | 0.005 | 0.003 | 0.001 |
| 430 (OK) | 1.4016 | 0.047 | 0.26 | 0.51 | 16.2 | 0.2 | 0.01 | 0.1 | | 0.001 | 0.004 | 0.002 |
| 439 | 1.4510 | 0.013 | 0.38 | 0.35 | 17.3 | 0.2 | 0.02 | 0.3 | 0.01 | 0.38 | 0.003 | 0.001 |
| 444 | 1.4521 | 0.014 | 0.44 | 0.37 | 17.8 | 0.1 | 2.0 | 0.02 | 0.02 | 0.17 | 0.27 | 0.001 |
| 201 | 1.4372 | 0.084 | 0.33 | 7.01 | 16.9 | 4.5 | 0.11 | 0.24 | 0.20 | 0.000 | 0.004 | 0.003 |
| 201Cu | | 0.049 | 0.29 | 5.6 | 17.2 | 4.7 | 0.21 | 2.3 | 0.11 | 0.000 | 0.005 | 0.002 |
| 204Cu | | 0.072 | 0.39 | 8.95 | 14.9 | 1.1 | 0.03 | 1.7 | 0.11 | 0.000 | 0.001 | 0.004 |
| 304 | 1.4301 | 0.044 | 0.51 | 1.47 | 18.2 | 8.2 | 0.15 | 0.3 | 0.02 | 0.002 | | 0.001 |
| LDX 2101 [®] | 1.4162 | 0.034 | 0.71 | 4.94 | 21.6 | 1.5 | 0.32 | 0.3 | 0.23 | 0.002 | 0.005 | 0.001 |

Table 1. The chemical compositions (wt%) of the stainless steels investigated. LDX $2101^{\mbox{\tiny (B)}}$ is an Outokumpu registered trade mark

Pitting Potential Measurements

A detailed description of the Avesta Multicell has been given by Berner et al. [12]. The potential was applied by a single standard Solartron 1287 potentiostat. Necessary electronics and software for controlling the experiment were built in-house. A crevice-free mount was achieved by flowing DI-water individually to each channel using an Alitea 403U/C6 peristaltic pump, giving a flow rate of 6 ml/hr. For temperature control, a Haake Phoenix II thermal controller was used. The sample surface and electrolyte temperatures were related by mounting stainless steel samples of different thicknesses with embedded PT-100 elements for a solution temperature range from 0 to 90 °C. However, when experiments are performed at 25 °C, as in this study, there is no temperature gradient and consequently no need for correlating the sample surface and solution temperatures.

Six samples were measured on each run, using a potentiodynamic routine inspired by the ASTM G 61 standard [5]. The electrolyte used was 1 M NaCl. The possibility to measure six samples during one test run is necessary to obtain sufficient statistics for a correct interpretation. By

adjusting the test temperature and electrolyte, this method can be adopted to suite a wide range of grades. The open circuit potential of the set of six samples was recorded for 15 minutes before sweep start from the open circuit potential. The scan rate was 10 mV·min⁻¹. When the current for a sample exceeded 1 mA·cm⁻², it was disconnected from the applied potential in order not to affect the others. The criterion for pit initiation was set to 100 μ A·cm⁻² for a duration of at least 60 seconds; the time criterion was imposed to filter out metastable pitting events. All potentials given in this paper are referenced to the Ag/AgCl reference electrode with a standard potential of 222.4 mV_{SHE} at 25 °C. The solution was deaerated with nitrogen gas during the entire experiment. All values reported are averages recorded on at least six samples.





Figure 1. The Avesta multicell in operation (left). To facilitate sample mounting, the cell can be turned upside down (right).

Results and Discussion

The average results of the pitting potential measurements of six samples are displayed in Fig. 2, where a higher pitting potential reflects a better resistance to localized corrosion. All samples were ground prior to analysis to estimate the bulk corrosion resistance and avoid differences associated with variations in surface finish.

The results obtained with the Avesta Multicell show good precision: 95% confidence intervals were found to be about ± 20 mV for most grades. A higher pitting potential is normally associated with a larger spread in the data. The standard deviation has been found to increase once the steel approaches its CPT; close to the CPT, a significant fraction of the samples will suffer from transpassive breakdown or local attack.

The pitting potentials of the competitor as well as the Outokumpu 430 materials were very similar: 194 ± 14 and 202 ± 21 mV, respectively. In the continued evaluation, these materials are treated as one lot.

As can be seen from Fig. 2, the following ranking of the steel grades in this paper could be obtained from the pitting potential measurements:

[444, 304, LDX 2101[®]] > [201, 201Cu] > 439 > [430, 204Cu]



Figure 2. Average pitting potentials measured with the Avesta multicell. Error bars estimates a 95% confidence interval (2σ) and are based on at least six measurements. The results for the two different lots of 430 are presented as one bar.

In the literature, a frequently quoted formula for the Pitting Resistance Equivalent Number (PREN) is

$$PREN = 1 \times [wt\%Cr] + 3.3 \times [wt\%Mo] + 16 \times [wt\%N]$$
(1)

The factor for nitrogen can vary significantly, but 16 and 30 are frequently cited values. In this paper, it was chosen to use the factor 16 for all steels. A recent compilation of works discussing the PREN and its application has been written by Szklarska – Smialowska [11]. Other formulae have also been suggested: for example, the pitting resistance equivalent has been applied to analyze the synergism between nitrogen and molybdenum [13].

The composition alone can not be used to predict the corrosion resistance. Other factors that have a strong influence include surface condition, inclusion density and other factors related to the microstructure. When inspected, no material in this study showed any deviations in microstructure. The importance of microstructure is illustrated by the fact that sputter deposited 304, with an average grain size of 25 nm, showed a pitting potential about 850 mV above that of conventional material [14].

Figure 3 shows a compilation of pitting potentials as a function of PREN calculated from equation (1). When inspecting the dataset, two trends can be seen: one for the lower range alloys, which contain only small amounts of nitrogen and molybdenum, and one for the higher alloy grades. One possible explanation is a nitrogen-molybdenum synergism that would become efficient only if both elements are present. This relation could also influence the regression for the high alloy end even if no explicit combined term is used, as suggested by Pettersson [13]. It is also interesting to note that two alloys, 430 and 204Cu, with the same low pitting potential also get the same PREN. The PREN formula is established using the widest alloy range possible, which gives a strong influence of high alloy grades in the linear regression.

This study has shown the Avesta Multicell to be a viable tool for ranking the corrosion resistance of some standard stainless steel grades using the pitting potential method. It can also be used to

record critical pitting temperatures (CPTs). This option opens up the possibility for wider comparisons of different types of samples on an industrial scale, e.g. to obtain rapid classification of weld procedures on special grades.



Figure 3. Pitting potentials as a function of the pitting resistance equivalent number (PREN).

Conclusions

- The Avesta Multicell provides fast and simple crevice-free mounting of flat samples for different types of pitting experiments: pitting potentials as well as critical pitting temperatures.
- When considering the standard pitting resistance equivalent formula, it fits well to the grades with higher resistance to localized corrosion (201, 201Cu, 304, 444, LDX 2101). The lower end grades (430, 204Cu) deviated from this trend.

Acknowledgements

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SENSITIZATION BEHAVIOUR OF MANGANESE-ALLOYED AUSTENITIC STAINLESS STEELS

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Abstract

Manganese is an essential alloying element in advanced austenitic stainless steels with specific properties such as high resistance to harsh corrosive environments, high strength or low material costs. These materials are often used for welded constructions which have to be highly corrosion resistant. Hence it has to be ensured that the heat input during welding does not initiate the precipitation of chromium carbide resulting in a susceptibility to intergranular corrosion. This leads to the question whether the sensitization behaviour of manganese-alloyed austenitic stainless steels is comparable to that of the well-known conventional chromium nickel austenites.

In the present work the effect of heat-input on the susceptibility of the CrNi-steel 1.4301 and the CrNiMn-steel 1.4376 to intergranular corrosion (IGC) was considered. Investigations were carried out by corrosion testing in the so-called Strauss-Test to elucidate the effect of the annealing temperatures on the microstructure. Furthermore, the influence of heat treatment on the mechanical properties was evaluated by tensile testing.

As a result, it could be demonstrated that manganese-alloyed austenitic stainless steels like grade 1.4376 exhibit a sensitization behaviour very similar to the conventional austenitic steel grades. The same kinds of tests on intergranular corrosion resistance can be applied for both types of materials.

Introduction

Metastable austenitic stainless steels have found increased interest in modern lightweight construction because they combine high strength values with good formability. This combination of properties results from the pronounced strain hardening of these materials, the metastable austenite largely transforms to martensite during cold-deformation.

Strength values can be further increased by partially substituting nickel by manganese thus enabling to achieve higher nitrogen levels. In doing so these materials get a very special basic composition and the question arose whether they also show a sensitization behaviour different from standard austenitic steels like 1.4301. Thus the steel grade 1.4376 was taken as an example for this steel group for investigating the effect of sensitizing heat inputs on the resistance to intergranular corrosion of this material.

Experimental

Table 1 gives the chemical composition of the two steel grades to be investigated (1.4376 and 1.4301).

| [wt%] | C | Si | Mn | Р | S | Cr | Ni | Мо | Ν |
|--------|-------|------|------|-------|-------|------|------|------|-------|
| 1.4376 | 0.039 | 0.41 | 6.54 | 0.025 | 0.004 | 17.8 | 4.25 | 0.17 | 0.195 |
| 1.4301 | 0.057 | 0.41 | 1.37 | 0.027 | 0.002 | 18.1 | 8,05 | 0.24 | 0.046 |

Table 1. Chemical composition of the steels investigated

Sheet samples of 100 mm x 15 mm x 1.5 mm from both materials were subjected to a sensitization treatment by annealing in a salt bath. Thereby annealing temperatures between 500 and 900°C (in steps of 50°) and exposure periods of 2, 4, 6, 8, 10, 12, 16, 30 and 60 min were chosen. After immersion in the salt bath, the samples were cooled in water. To make allowance for the influence of heating and cooling rates, comparative samples were annealed for analogous time periods in a laboratory kiln at 700°C and subsequently cooled in air. In order to remove impurities or eventual oxidation products, the surfaces of the sensitized samples were ground with SiC paper (P120) and cleaned in an ultrasonic bath in ethanol afterwards.

The Strauss test according to the standard EN ISO 3651-2 Method A was used for evaluating the resistance to intergranular corrosion: The test samples were exposed to a boiling aqueous solution prepared from 100 g of CuSO₄•5H₂O and 184 g of H₂SO₄ (16%) per liter containing about 60 g of copper chips. After 20 h of exposure time, the samples were removed and thoroughly rinsed with deionized water. Then the sheet samples were bent to 90°. The bent region of the samples was analysed by Scanning Electron Microscopy (SEM). Thereby samples were selected for further investigation by metallographic preparation and optical microscopic characterization.

Tensile testing was performed on samples of 1.4376 and 1.4301 according to standard EN 10002-1 (sample geometry DIN $50125 - E 1,47 \times 10 \times 22$). Prior to the testings, the samples were subjected to a sensitizing annealing treatment at 600, 700 and 800°C respectively for 48 min. Five analogous samples were treated under the same conditions. In addition, unannealed samples were tested for comparison.

Results and Discussion

Strauss Testing

The corrosive attacks observed by optical microscopy were classified into four degrees. The first does hardly reveal any attack (Figure 1). In the second case, several grains are partly dissolved at the surface, however definite intergranular corrosion (IGC) attack cannot be corroborated (Figure 2). Figure 3 gives an example of stronger corrosion attack (of about 50 to 100 μ m depth) along the grain boundaries which can clearly be interpreted as IGC. The most pronounced degree of corrosion is shown in Figure 4 with an attacking depth of at least 100 μ m.



Figure 1 (left). Metallographic picture of a bent 1.4376 sample, annealed in a salt bath of 700°C for 6 min Figure 2 (right). Metallographic picture of a bent 1.4376 sample, annealed in a salt bath of 650°C for 60 min



Figure 3 (left). Metallographic picture of a bent 1.4301 sample, annealed in a salt bath of 700°C for 60 min Figure 4 (right). Metallographic picture of a bent 1.4301 sample, annealed in a salt bath of 650°C for 60 min

An evaluation of the optical microscopic analysis of the microstructures of 1.4376 and 1.4301 is given in the Figures 5 and 6, which exhibit the various degrees of attack observed in a schematic plot of annealing time and temperature. Considering the susceptibility to corrosive attacks along the grain boundaries, the behaviour of 1.4376 is positively shifted towards lower annealing temperatures and towards longer annealing times compared to 1.4301. While significant IGC is observed with 1.4301 after annealing at 650 to 700°C for 16 to 30 min, 1.4376 shows severe attack only after 60 min annealing at 600°C. The comparison of the samples annealed at 700°C in the laboratory kiln reveals no significant difference from the samples annealed in the salt bath, which indicates a minor influence of heating and cooling rates. However, as only one annealing temperature (700°C) was compared, which moreover lies beyond the susceptibility of 1.4376, a generally valid statement about the influence of heating and cooling rates is not possible.

The investigations by Scanning Electron Microscopy (SEM) were employed at first for the evaluation of the corrosive attacks visible on the surface, and moreover to select representative samples for metallographic preparation. The documentation by SEM, which gives only an analysis of the sample surface, is not valuable for a description of the kind and depth of the corrosion attack. Though in case of pronounced intergranular attacks along the grain boundaries, the bent surface reveals dissected grains beneath the dehisced surface in some places and thus gives reason to assume intergranular attack. In Figure 7 a such example is demonstrated. The actual, deeper reaching attack can be corroborated by the respective metallographic picture (Figure 3). However not in every case a deeper corrosion attack can be concluded from cracks

along the surface detected by SEM (Figure 8), as only marginal surface attack is demonstrated by the respective metallographic analysis (Figure 9).



Figure 5. Influence of annealing time and temperature on the sensitization behaviour of 1.4376



Figure 6. Influence of annealing time and temperature on the sensitization behaviour of 1.4301



Figure 7. Surface of a bent 1.4301 sample, annealed in a salt bath of 700°C for 60 min (SEM, 5000x)



Figure 8 (left). Surface of a bent 1.4301 sample, annealed in a salt bath of 750°C for 60 min (SEM, 5000x) Figure 9 (right). Metallographic picture of a bent 1.4301 sample, annealed in a salt bath of 750°C for 60 min

Tensile Testing

From the σ - ε curves obtained, the materials characteristic values were determined. The average from five respective measurements is given in Table 2. The yield strength at 0.2% ($R_{p0.2}$) as well as the ultimate tensile strength (R_m) reveal significantly higher values for 1.4376 compared to 1.4301, whereas the maximum uniform elongation (A_G) and the elongation before rupture (A_5) obtained from 1.4376 are clearly lower. These results seem quite obvious in consideration of the metastable austenitic structure of the grade 1.4376.

| average value from 5 measurements | | 0.2% yield strength R _{n0.2} [N/mm ²] | tensile strength <i>R_m</i> [N/mm ²] | elongation before rupture A_5 [%] | maximum uniform elongation A _G [%] |
|--------------------------------------|---------------|--|---|---|---|
| | unannealed | 290.8 | 673.5 | 57.0 | 46.2 |
| 1 4201 | 600°C / 48min | 292.2 | 675.5 | 56.6 | 46.2 |
| 1.4501 | 700°C / 48min | 281.4 | 678.6 | 55.7 | 46.4 |
| | 800°C / 48min | 278.8 | 685.5 | 55.0 | 47.2 |
| | unannealed | 443.6 | 790.8 | 49.6 | 36.8 |
| 1 4276 | 600°C / 48min | 430.2 | 783.4 | 49.4 | 37.2 |
| 1.4376 | 700°C / 48min | 421.2 | 787.0 | 50.0 | 39.1 |
| | 800°C / 48min | 413.8 | 783.4 | 52.6 | 41.3 |

Table 2. Materials characteristic values from tensile testing on 1.4301 and 1.4376

As for the influence of the annealing temperature on the materials characteristic values, despite relatively small alterations, a different behaviour is observed for the two steels: The ultimate tensile strength (R_m) of 1.4301 is increased with increasing annealing temperature. The steel 1.4376 exhibits comparably higher values, however, a definite influence of the temperature cannot be determined. Considering the values of the elongation before rupture (A_5), higher annealing temperatures cause a decrease for 1.4301, but an increase for 1.4376. At last, increasing annealing temperatures also lead to a decreasing yield strength ($R_{p0.2}$) and to an increasing maximum uniform elongation (A_G) for both steels.

Overall, for both steels 1.4301 and 1.4376, the resistance against plastic deformation tends to be reduced towards higher annealing temperatures. Though, as an effect of the annealing treatment, a slight hardening is observed with 1.4301, whereas the steel 1.4376 exhibits a reduction in strength.

The differing properties as a consequence of the annealing treatment observed for the two materials investigated, at one hand corroborate the results obtained from the Strauss Testing, which revealed a higher susceptibility to intergranular corrosion for 1.4301. In particular, the hardening effect of 1.4301 can be interpreted as a result of carbon accumulations along the grain boundaries. On the other hand, the deviations between samples annealed at different temperatures are relatively small and thus do not imply a significant influence of the annealing temperature.

Conclusions

Sheet samples of the two steel grades 1.4376 and 1.4301 were sensitizised by annealing at temperatures between 500 and 900°C for 2 to 60 min in a salt bath with subsequent cooling in water. The investigation of the samples in the Strauss Testing revealed a detectable intergranular corrosion (IGC) attack for 1.4301 after a sensitization of the steel for 16 to 30 min at 650 to 700°C. In comparison, the susceptibility of 1.4376 to IGC is shifted towards longer annealing times, but to slightly lower annealing temperatures: pronounced intergranular attacks could be observed after a sensitization treatment of 60 min at 600°C. This different susceptibility to sensitizing heat impacts can be referred to the different carbon levels of the materials tested. So the 1.4376-material with only 0.039 % C tolerated longer heat exposure periods than the steel 1.4301 tested containing 0.057 % C. A distinct influence of the basic steel composition (CrNi- or CrMnNi-type) could not be observed. Apparently the high manganese content of the grade 1.4376 has at least no pronounced negative effect on the sensitization behaviour of this alloy. In consideration of the heating and cooling rate of the annealing treatment, comparative samples were heated in a laboratory kiln (700°C, 48 min) and subsequently cooled in air. No significant difference could be seen compared to the water-cooled samples, which demonstrates that no particular influence of the heating and/or cooling rate is present in the range investigated.

To evaluate the effect of sensitization on the mechanical properties of the steels, tensile testing was performed on unannealed and annealed samples (600 to 800°C, 48 min) of both steels 1.4376 and 1.4301. As a result, significantly higher strength and lower elongation values were observed for 1.4376 compared to 1.4301, which is in agreement with the materials composition. As a striking issue, the strength is slightly increasing for 1.4301, but decreasing for 1.4376 in consequence of the sensitization treatment. This effect might be caused by carbon accumulation along the grain boundaries due to the heat treatment. However, the differences between the values obtained from different annealing temperatures are small, i.e. the heat treatment has a minor influence of the mechanical properties of the materials investigated.

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