

Corrosion properties of UNS S32101

– Reinforcement bar

Dear Reader

To some extent, following the concept of duplex grades presented in the previous issue, also this Acom will cover the use of duplex stainless steels, but this time emphasising the use of it for reinforcement bars.

The grade in question, LDX 2101, was described also in the previous issue as a new grade, which already has created a huge interest for certain applications, not least within civil engineering. And of course, reinforced concrete structures play a very important role for civil engineering independent of if it is a matter of house building, base structures for industrial buildings, hydropower dams or bridges to mention a few.

I normally don't have pictures on the front cover of Acom, but considering the subject discussed I cannot resist the temptation this time. The photo shows two piers built at two different occasions and there are no doubts that the stainless option resulted in less requirements for maintenance. The grade used was 1.4301 (304).



Concrete piers with mild steel re-bars after 32 years of service (left) and stainless steel re-bars after 60 years (right) (Courtesy of Nickel Institute).

LDX2101 has far better corrosion resistance than 1.4301 as shown in this article and it has more than twice the strength.

Enjoy the reading and have a serious look upon stainless re-bars, preferably in duplex LDX 2101, the next time you are going to build a bridge or power plant dam or whatever your interest is.

Yours sincerely

Jan Olsson

Technical editor of Acom

Corrosion properties of UNS S32101

– a new duplex stainless steel with low nickel content tested for use as reinforcement in concrete

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Abstract

A new duplex stainless steel, S32101, was chosen in this work for investigation of the corrosion resistance in an environment corresponding to concrete pore solutions. The new duplex stainless steel was developed for general use and with high mechanical strength. Furthermore, the steel has a chemical composition implying a corrosion resistance similar to that of type 304 or better. To balance the austenitic-ferritic microstructure nitrogen and manganese are used instead of expensive nickel. In this work a general screening of the corrosion resistance of this steel grade is presented. First, this includes results from a test program regarding uniform corrosion, where a number of steel grades in addition to the new duplex steel grade were tested according to a test program specified by the Materials Technology Institute, MTI and standardized as ASTM G 157. Then, results from laboratory corrosion tests regarding pitting corrosion, intergranular corrosion and stress corrosion cracking were compared for the new duplex steel to the standard austenitic stainless steels. Finally, the suitability of using this new duplex steel as reinforcements in concrete was investigated. For this purpose, rebars of UNS S32101 were compared with standard stainless steels, using electrochemical tests to screen the corrosion resistance. The test solutions were artificial solutions corresponding in alkalinity and chloride contents to concrete pore solutions. High corrosion resistance was obtained for the new duplex stainless steel in these solutions. These results were also discussed and compared with a field test carried out in a concrete bridges-survey.

Introduction

Reinforcement bar is a rather new application for stainless steel. Some examples of stainless steel grades used as reinforcements in concrete are of type 304, 304N, 316LN austenitic steel grades and UNS S32205, a duplex stainless steel grade with higher strength. The objectives, at present time, for alternative materials in reinforcements are improvement of properties and cost reduction. In this study the corrosion properties of a new duplex stainless steel grade LDX 2101[®] [1], UNS S32101 (EN1.4162) are presented.

The cost saving potential of using stainless steel S32101 as, for example, reinforcements in concrete, where high strength can be utilized and good corrosion performance is emphasized can be illustrated by good corrosion resistance and in less effort in maintenance.

Localized corrosion such as pitting or crevice corrosion is rather expected in an environment containing chlorides, but commonly the high pH (>12) in concrete is beneficially increasing the corrosion resistance of stainless steels. For uniform corrosion to occur the environment has to be very acidic. Uniform corrosion might also occur in an alkaline environment in combination with a high temperature (100°C). However, in due time aging of concrete will introduce carbonation when SO₃ and CO₂ from rainwater penetrate the concrete and the pH is lowered close to 10 [1]. Nevertheless, in a concrete pore solution at this high pH the stainless steel would remain in the passive state. Chlorides are also present due to several possible causes such as deicing salts, chlorides in the mixing water for the concrete or any marine environmental influence. The chloride can either be bound into the concrete but also remain as free chlorides in the pore-solution. Calculating the risk for corrosion the amount of free chlorides in the

pore-solutions has to be taken into account. Wang and Newman, recently investigated the possibility for crevice corrosion to occur on a steel grade of type 316L in concrete pore solutions at various high pH. For rebars the crevice situation is likely to occur due to the attachment of the concrete. However, the authors showed that any natural initiation process for crevice corrosion was slow or even impossible due to a low corrosion potential in alkaline solutions [2]. Results from a field study carried out by the Swedish Corrosion Institute, performing corrosion studies of partly cast-in test bars of stainless steels showed no corrosion, neither uniform or localized on any of tested steel grades after a year field exposure on the Öland bridge, located in brackish marine environment and exposed to de icing salts during winter time [3]. The stainless steels tested were the austenitic grades 304L and 316L and the two duplex grades S32101 and S32205, 12 bars of each grade. Six test bars of twelve, from each stainless steel grade were electrically connected to the cast-in steel reinforcement of the edge beam, to study the influence of galvanic corrosion.

Over the last two decades, a number of cases have shown the advantage of implementing duplex stainless as a construction material. The mechanical properties of S32101 compared with a steel grade type 304L stainless steel are given in table 1 at 20°C. There is a pronounced difference between the austenitic grade, 304L and the duplex stainless steel grade, i.e. S32101. However, there is no major difference in the elasticity (Young's modulus), which is around 200 GPa for both grades at room temperature and which drops only a few percent up to 200°C.

Mechanical properties of steel grade type 304L and S32101.

Table 1

| ASTM | EN | EN, min values | | | ASTM, min values | | |
|--------|--------|----------------|-------------|-----------|------------------|-------------|-----------|
| | | Rp0.2 (MPa) | Rm (MPa) | A5 (%) | Rp0.2 (MPa) | Rm (MPa) | A5 (%) |
| 304L | 1.4307 | 200 | 500 | 45 | 170 | 485 | 40 |
| S32101 | 1.4162 | 450 | 650 | 30 | 450 | 650 | 30 |

Stainless steel and corrosion

There are several corrosion forms depending on the environment and steel grade in combination. Environments causing uniform corrosion on stainless steels are primarily very strong acids but also hot (>110°C) alkaline environments. Generally the increase of the amount of alloy elements such as chromium and molybdenum increases the resistance to general corrosion. The general corrosion resistance of different steel grades is basically measured in the laboratory by immersion in the compound in question and measuring the weight loss after a specified time of exposure.

Environments causing pitting corrosion or crevice corrosion are commonly neutral solutions containing high amounts of chlorides. Chromium, molybdenum and nitrogen are the most essential elements for the resistance to local corrosion of stainless steels. The Pitting Resistance Equivalent, PRE, is calculated on the basis of the composition of the alloy and gives information on the relative pitting corrosion resistance of the stainless steel grade according to:

$$PRE = \%Cr + 3.3\%Mo + 16\%N$$

When introducing a new material the corrosion resistance to most corrosion forms is tested, such as the above mentioned but also for stress corrosion cracking and intergranular corrosion. A risk for stress corrosion cracking for austenitic standard steel

grades in chloride environment is well known at higher temperatures above 50°C under evaporative conditions. However, a super austenitic or super duplex stainless steel performs better regarding SCC. We know by experience that a duplex stainless steel shows higher resistance to stress corrosion cracking versus a similar austenitic steel grade. Intergranular corrosion is rare for new types stainless steel grades due to the low carbon content. Nevertheless, based on these circumstances, stress corrosion cracking or intergranular corrosion would not be expected corrosion forms for rebars in concrete environments.

Experimental

Material

The test materials were standard austenitic stainless steel grades, 304, 316L, and a duplex stainless steel grade, S32101. The typical chemical compositions, PRE values and microstructure for tested stainless steel grades are presented in table 2. The stainless steel grade S32101 was tested as two samples configuration, one as base material from plate and another as hot rolled rebars with as received, i.e. pickled surfaces from the manufacturing process. The reference samples were chosen to compare the corrosion properties of S32101 with standard austenitic stainless steels and not preferably to other steel grades used in reinforcements.

Steel grades used in the laboratory tests.

Table 2

| Material | | | Typical compositions weight-% | | | | | | Micro structure |
|------------|--------|-----|-------------------------------|-------|------|------|------|-------|-----------------|
| ASTM | EN | PRE | Cmax | Cr | Ni | Mo | N | Other | |
| S32101 | 1.4162 | 26 | 0.04 | 21 | 1.35 | 0.1 | 0.20 | Mn(4) | Duplex |
| 304 | 1.4301 | 19 | – | 18.47 | 8.60 | 0.25 | – | | Austenitic |
| 316L | 1.4404 | 24 | 0.03 | 16.5 | 10 | 2 | – | | Austenitic |
| 316L (hMo) | 1.4432 | 26 | 0.03 | 16.5 | 10.5 | 2.5 | – | | Austenitic |

Uniform corrosion according to a standard guide for evaluating the corrosion properties of nickel- and iron based alloys, ASTM G 157

ASTM G 157-98 specifies fourteen environments for evaluating general corrosion resistance of nickel- and iron based alloys, regardless of manufacturing source. UNS S32101 was tested in thirteen of these solutions and compared with standard grades 304 and 316L. All solutions were made from reagent grade chemicals. At temperatures below the boiling point the oxygen in the test solutions was purged with high purity nitrogen. The corrosion resistance was determined in these test solutions at various temperatures to determine the critical temperature, i.e. the lowest temperature at which the corrosion rate exceeded 0.13 mm/y (5mpy). The interval between the test temperatures was 5°C. The compositions of the test solutions specified by ASTM G 157-98 are shown in table 3. The test solutions containing 5.0 w-% of hydrochloric acid were excluded due to that these solutions were considered much too corrosive for relevant results for tested steel grades. Weight loss measurements were carried out with parallel coupons exposed for 96 hours. The critical temperature reported were derived from the least resistant specimen. In addition, control alloys supplied by MTI, are included in most tests and reported below the relevant tables.

The test coupons, measuring 20 x 50 mm, were cut with their length in the rolling direction. The edges were machined to a depth corresponding to the thickness of the coupon. All surfaces were finally ground with dry No. 120 grit abrasive paper.

Test solutions specified by ASTM G 157-98

Table 3

| Corrodent | Formula | Concentration, w-% |
|-------------------------------------|---|---------------------------------|
| Hydrochloric acid | HCl | 0.2, 1.0, 5.0 |
| Sulfuric acid | H ₂ SO ₄ | 10, 60, 96 |
| Nitric acid | HNO ₃ | 10, 70 |
| Phosphoric acid | H ₃ PO ₄ | 85 |
| Formic acid | HCOOH | 50 |
| Acetic acid | CH ₃ COOH | 80 |
| Sodium hydroxide | NaOH | 50 |
| Hydrochloric acid + Ferric chloride | HCl + FeCl ₃ | 1.0 HCl + 0.3 FeCl ₃ |
| Acetic acid + Acetic anhydride | CH ₃ COOH +(CH ₃ CO) ₂ O | 50/50 |

Pitting Corrosion, Critical Pitting Temperatures (ASTM G 150)

The Critical Pitting Temperatures, CPT, were determined as prescribed in ASTM G 150 in 1 M sodium chloride solution at a constant potential of +700mV/SCE. The standard prescribes that the testing should be performed in such a way that simultaneous crevice corrosion is avoided. For that reason, the Avesta cell was used. This electrochemical cell is described in the ASTM G 150 standard as the Flush Port Cell. The test cell volume was around 1 liter. The standard test area chosen for the potentiostatic procedure was 10 cm². The temperature of the specimen was increased by a rate of 1°C/min, starting from 0°C. CPT was defined as the temperature at which the current density exceeded 100 μA/cm². For the screening of CPT, surfaces, wet ground to 320 mesh were used.

The manufacturing of rebars normally involves rolling at such a rate that the material will become red hot and cooled in air afterwards. A pitting corrosion test was also performed to check if the material after such a treatment was less corrosion resistant than material that was properly annealed and quenched as a final operation. This test was performed on cross sections of 16 mm material with the test method described above.

The CPT was also measured according to ASTM G 150 on cross- sections of rebars of stainless steel S32101 using the Avesta cell. The sample area for these measurements was, however, 1 cm².

Crevice Corrosion, Critical Crevice Temperatures (modified ASTM G48 D)

The resistance to crevice corrosion was measured as the Critical Crevice corrosion Temperature (CCT) in accordance with a modified version of ASTM G48 D, i.e. in a solution containing 5% ferric chloride and 1% sodium nitrate. The nitrate has inhibitive effects on corrosion of stainless steel, which created a less aggressive solution. The crevice formers were of MTI-type and the torque was 0.28 Nm. The exposure time was 24 hours.

Stress Corrosion Cracking

Stress corrosion cracking was tested according to ASTM G 157-98 using 4-point loaded specimens with a stress level of 90% of the proof strength at 100°C in 4 M (19.5%) magnesium chloride. The test period was 500 hours.

Electrochemical dynamic polarization measurements

Anodic dynamic polarization measurements were carried out in pore-solutions manufactured in the laboratory similar to solutions reported to simulate pore-solutions in concrete [1]. The scan rate was 20 mV/min and the breakdown potential was determined from the current value exceeding continuously 10 $\mu\text{A}/\text{cm}^2$. The breakdown potential was calculated as the mean value from measurements of parallel samples. The corrosion potential was measured before the polarization scans after ten minutes of samples in immersion.

Furthermore measurements were carried out to measure the corrosion potential continuously for rebar of steel grade S32101 in the worse pore-solution containing the highest amounts of chlorides. The solution was for the continuous measurements, stagnant with no stirring and in continuous contact to air. No de-aeration actions were taken before or during these measurements. All electrochemical potential measurements in this work were carried out versus the saturated calomel electrode (SCE).

The test cell used for reference samples as plate was the Avesta cell, i.e. flush port cell and the sample area was 1 cm^2 . The polarization measurements on the rebars were carried out on the rebars immersed vertically in the pore-solution and nitrogen gas purged in the gas fill to avoid water line corrosion. The cut end of the rebar was masked with and hydrophobic silicon, Provil H by Heraeus Kulzer to avoid crevice corrosion and to receive measurements on the mantle surfaces and not the cut end. The rebars were of two dimensions 1.5 cm and 2.0 cm in diameter. The length of the samples immersed into the pore-solution was ~5 cm for all samples, providing a sample area of 24 cm^2 for the thinner bars and 31 cm^2 for the thicker bars. Figure 1 shows schematically the experimental setup for electrochemical measurements of rebars and figure 2 shows the rebars of S32101 before tests.

Dynamic polarization measurements were also carried out in 0.1 M NaCl, de aerated, to determine the breakdown potentials at various temperatures for steel grades type 304, 316L and S32101.

Pyc propose a basic pore-solution for measurements in the laboratory, which was also used according to the following composition: 0.4 M KOH, 0.2 M NaOH and 0.004 M $\text{Ca}(\text{OH})_2$ [1]. The measurements were carried out under ambient temperature (22°C). Chlorides were added to the pore-solutions in the amounts of: 1 g/L, 10 g/L, 21 g/L and 42 g/L. The pH of the test solutions was between 13.0 and 13.5.

Fig. 1 Experimental setup for electrochemical measurements on rebars.

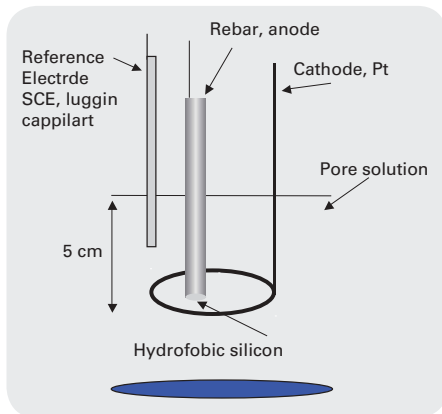


Fig. 2 Rebars of steel grade UNS S32101 (EN 1.4162) prior tests.



Results

Corrosion properties of duplex steel grade S32101

Uniform corrosion: The critical temperatures determined in the different test solutions are shown in tables 4 to 8. In some cases corrosion other than uniform corrosion was observed. These cases were marked with “p” (pitting corrosion on the face of the specimens) in connection with the critical temperatures. Below the tables the corrosion rates of the control alloys for the specific solutions according to test numbers, are presented at the temperatures prescribed by MTI. In the tests where the boiling point, bp, was reached the measured temperature is reported in connection with the control alloy results.

Uniform corrosion in hydrochloric acid solutions.

Table 4

| Test solution | Test No | Conc. w-% | Critical temperature, °C | | |
|-------------------------|---------|---------------------------------|--------------------------|-----|--------|
| | | | 316L | 304 | S32101 |
| HCl | 1 | 0.2 | >bp | >bp | >bp |
| HCl | 2 | 1.0 | 30 | 30p | 55 |
| HCl + FeCl ₃ | 3 | 1.0 HCl + 0.3 FeCl ₃ | 25p | 20p | 20 |

MTI Control Test No 1, UNS 304, 90°C, 0.23 mm/y, p, bp 100°C

Uniform corrosion in sulfuric acid solutions.

Table 5

| Test solution | Test No | Conc. w-% | Critical temperature, °C | | |
|--------------------------------|---------|-----------|--------------------------|------|--------|
| | | | 316L | 304 | S32101 |
| H ₂ SO ₄ | 4 | 10 | 50 | N.T. | 75 |
| H ₂ SO ₄ | 5 | 60 | <15 | N.T. | <<30 |
| H ₂ SO ₄ | 6 | 96.4 | 45/1 | N.T. | 30 |

MTI Control Test No 6, UNS 304, 30°C, 0.12 mm/y
N.T. Not tested**Uniform corrosion in phosphoric acid solutions.**

Table 6

| Test solution | Test No | Conc. w-% | Critical temperature, °C | | |
|--------------------------------|---------|-----------|--------------------------|-----|--------|
| | | | 316L | 304 | S32101 |
| H ₃ PO ₄ | 7 | 85 | 95 | 80 | 100 |

Uniform corrosion in nitric acid solutions.

Table 7

| Test solution | Test No | Conc. w-% | Critical temperature, °C | | |
|------------------|---------|-----------|--------------------------|-----|--------|
| | | | 316L | 304 | S32101 |
| HNO ₃ | 8 | 10 | >bp | >bp | >bp |
| HNO ₃ | 9 | 65 | 100 | 100 | 105 |

Test No, 8, bp 100°C

Uniform corrosion in organic acid and in sodium hydroxide.

Table 8

| Test solution | Test No | Conc. w-% | Critical temperature, °C | | |
|-------------------------------------|---------|-----------|--------------------------|------|--------|
| | | | 316L | 304 | S32101 |
| CH ₃ COOH | 10 | 8 | >bp | 100p | >bp |
| CH ₃ COOH | 11 | 50 | 120 | >bp | 105 |
| (CH ₃ CO) ₂ O | | 50 | | | |
| HCOOH | 12 | 50 | 40 | <10 | 95 |
| NaOH | 13 | 50 | 90 | 85 | 85 |

MTI Control Test No. 10 UNS 304, 90°C, 0.15 mm/y, p, bp 106°C

11 UNS 304, 100°C, 0.20 mm/y,p, bp 126°C

13 UNS 304, 90°C, 0.12 mm/y, bp 144°C

Pitting Corrosion: As reference, breakdown potentials were measured in 0.1 M sodium chloride solution at different temperatures for steel grades type 304, 316L and S32101, figure 3 shows received pitting potentials at different temperatures for austenitic steel grades 304 and 316L and figure 4 shows the received breakdown potentials for the duplex steel grade UNS S32101.

Fig. 3 Breakdown potentials, E_{p10} , vs. temperature for the austenitic steel grades in the 0,1M NaCl solution.

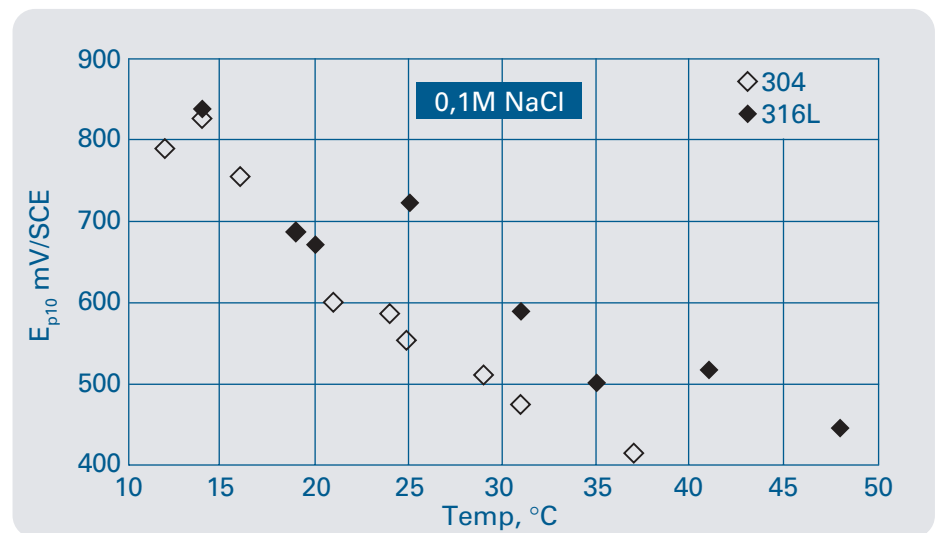


Fig. 4 Breakdown potentials, E_{p10} , vs. temperature for the duplex steel grade S32101 in the 0,1M NaCl solution.

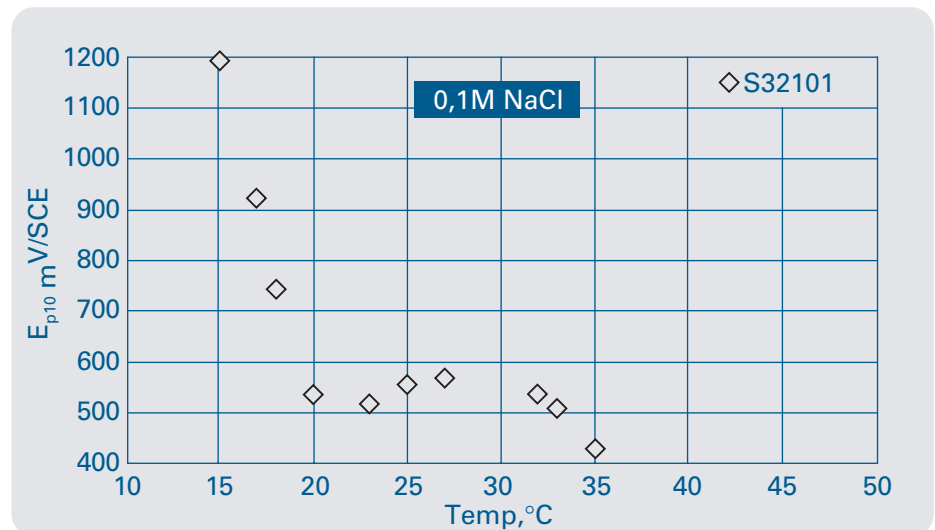


Figure 3 and 4 show that the duplex stainless steel grade S32101 shows similar pitting corrosion resistance as at least a stainless steel of type 304, since the scatter between the breakdown potentials between these steel grades can be explained by electrochemical statistical effects. In figure 4 the breakdown potential is stabilized or almost increased at temperatures between 20 and 30°C. The reason for this is not revealed by this investigation but has to be more thoroughly investigated.

The Critical Pitting Temperature measured according to ASTM G 150 for S32101, 316L and 316L (high molybdenum) is presented in table 9. Table 9 shows also measured CCT for these steel grades. It should, however, be noted that these two types of measurements are results from two different methods in two types of environments. The CCT was measured in a modified ASTM G 48 D in ferric chloride and the CPT in sodium chloride. Furthermore of major importance, the CCT is measured in a solution containing inhibitive nitrate and therefore shows a higher CCT than the CPT for all measured steel grades. Nevertheless, comparably with the other the steel grades, the S32101 has fairly good pitting resistance and crevice corrosion resistance, in full accordance with its PRE number.

CPT and CCT for UNS S32101 compared with steel grades 316L and 316L (high Molybdenum)

Table 9

| Material | S32101 | 316L | 316L(hMo) | Method |
|----------|--------|------|-----------|---------------------|
| CPT, °C | 21 | 16 | 18 | ASTM G 150 |
| CCT, °C | 45 | 20 | 30 | ASTM G48 D modified |

Table 10 below gives a summary of several CPT measurements on stainless steel grade S3201 on cross sections of rebars on pickled stainless steel.

Results from testing according to ASTM G 150 in 1M NaCl.

Table 10

| S32101 | CPT, °C |
|--------------------------|---------|
| Non-annealed 16 mm rebar | 11 – 14 |
| Fully annealed 16 mm bar | 17 – 19 |

Stress Corrosion Cracking: Many test methods are used to rank the different steel grades with respect to their resistance to SCC. The method used here is described in the MTI Manual no. 3 also standardized as ASTM G 157. In this test U-bent specimens were cut longitudinally as well as transversely to the rolling direction. The steel grade S32101 showed good resistance to chloride induced stress corrosion cracking, SCC, only superficial selective corrosion was occurred in the ferrite phase on S32101. The results are shown in table 11.

Results from SCC testing of U-Bends in 3M MgCl₂ at 100°C for 500 hours.

Table 11

| Material | Longitudinal/Transverse |
|----------|---|
| S32101 | No SCC, (some superficial selective corrosion of the ferrite phase) |
| 304 | SCC and pitting corrosion |

Intergranular corrosion: Duplex stainless steels are generally very resistant to intergranular corrosion and S32101 is no exception. A test method often used for delivery testing is described in the standard EN ISO 3651-2, and for steel grades with the S32101 composition, the sulfuric acid/copper sulfate test, Method A, is proposed. The results from this test showed no intergranular corrosion and accordingly S32101 passed this test. S32101 was also tested in the sulfuric acid/ferric sulfate test according to EN ISO 3651-2, Method C. This is a test method proposed for delivery testing of higher alloyed steel grades. Nevertheless, S32101 passed also this test without any remarks.

Corrosion properties of rebars of S32101 in pore solutions containing chlorides

The corrosion potential, E_{corr} was measured prior all electrochemical polarization measurements after 10 minutes in immersion of steel grade S32101 in pore-solutions containing various amounts of chlorides. Table 12 shows the results from these measurements.

Corrosion potential, E_{corr} for UNS S32101 in pore solutions containing chlorides.

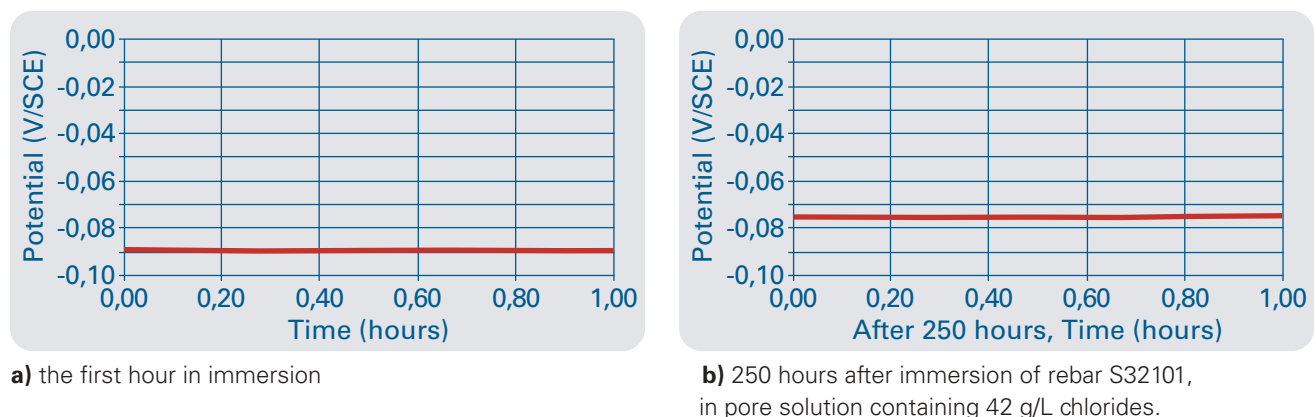
Table 12

| Chloride amounts in pore solutions g/L | E_{corr} after 10 minutes immersion of S32101, V/SCE |
|--|---|
| 1 | -0.210 |
| 10 | -0.056 |
| 21 | -0.200 |
| 42 | -0.089 |

The corrosion potentials, E_{corr} , varied in the range between -0.210 to -0.056, which indicates a large scattering. The scattering showed no dependence with the chloride content. Possible reasons to such a large variation is the variation in electrochemical properties of the stainless steel, which is dependent of for example variation in the surface oxide but also oxide content of the solutions in combination with pH. However, most important for corrosion of stainless steel in an neutral or alkaline environment is that the corrosion potential remains low for a period of long time and does not exceed the breakdown potential for the material. In an acid environment the low corrosion potential indicates uniform corrosion.

Continuous measurements of the corrosion potentials, E_{corr} , were also carried out for 250 hours on rebar of steel grade S32101. Figure 5 shows these measurements for the first hour in pore solution containing 42 g/L of chlorides and also after 250 hours. The corrosion potential increased in minor extent. As can be seen from the results only minor variation was obtained during the measurements since the potential increased from -0.0897 to -0.0751 V/SCE in 200 hours.

Fig. 5 Corrosion Potential, E_{corr}



A number of polarization measurements were carried out in pore solutions containing very high amounts of chlorides. The breakdown potentials were noted for the various chloride contents in the pore solutions at ambient temperature and table 13 shows the potential variations between the breakdown potentials for rebars of S32101 compared with both 304 and 316L in the various chloride containing solutions. The values were very similar between the steel grades and also almost independent on the amount of chlorides between 1 g/L to 42 g/L indicating the strong influence of the alkaline environment.

Breakdown potentials in pore solutions of steel grades 304, 316L and rebars of S32101

Table 13

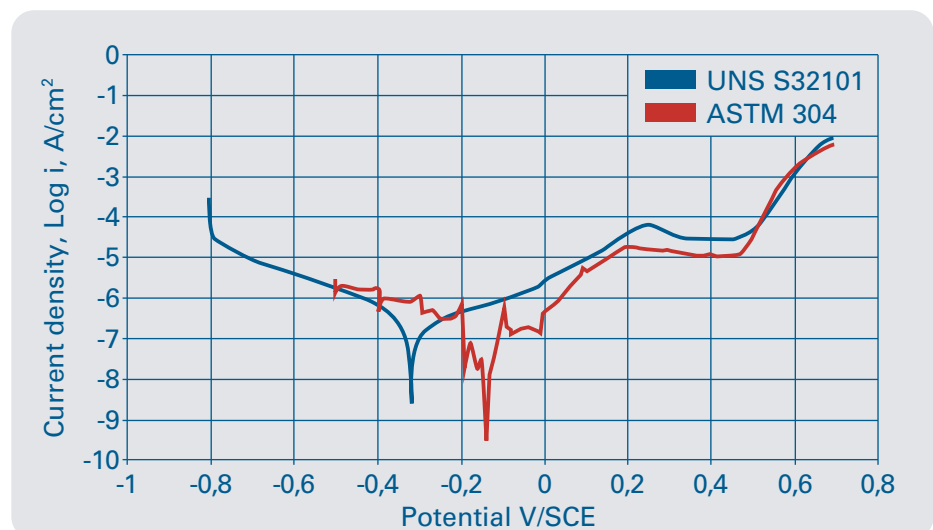
| Materials | Measured surface areas | Breakdown potential area for pore solutions containing 1, 10, 21 and 42 g/L chlorides V/SCE |
|--------------|------------------------|---|
| 304 plate | 1 | 0.608-0.635 |
| 316L plate | 1 | 0.604-0.623 |
| S32101 rebar | 24, 31 | 0.620-0.635 |

For the stainless steel grade S32101 in pore solution containing 42 g/L chlorides the breakdown potential was measured to 0.611 V/SCE. Commonly any of the steel grades tested would suffer from localized corrosion such as pitting corrosion in solutions containing these high amounts of chlorides due to a high corrosion potential, E_{corr} . However, due to the alkalinity the corrosion potential, E_{corr} is rather low (< -0.2 V/SCE) far away from the potential area where there is a risk for pitting corrosion. Figure 6 shows the anodic polarization measurements of a rebar in the most corrosive pore solution containing 42 g/L of chlorides. Breakdown of the passive film, i.e. corrosion is revealed by a high current density, $>10 \mu\text{A}/\text{cm}^2$. Figure 5b shows the corrosion potentials measured continuously for rebar of S32101 after 200 hours indicating that it is not likely that the corrosion potential will move close to the breakdown potential without any chemical or electrochemical polarization in the positive direction. Figure 6 shows for comparison the polarization measurements for 304 and S2101 in pore solution containing 42 g/L chlorides. The measurements show no active corrosion at lower potentials but only an indication of higher current densities in the cathodic potential area, at lower potentials than -0.8 V/SCE for UNS S32101.

Fig. 6 Anodic polarization measurements of rebar of steel grade S32101, diameter 2 cm, in pore solution containing 42 g/L chlorides.



Fig. 7 Rebars of S32101 after exceeding the breakdown potentials in pore solution containing a) 1 g/L chlorides and b) 10 g/L chlorides.



Whenever the breakdown potential was exceeded the corrosion started in the boundary between the silicon masking the end of the bar and propagated below the silicon seal similar to crevice corrosion. Nevertheless the attack seemed to start from the outside of the seal due to edge effects rather than crevice corrosion. Figure 7 shows corrosion on samples after the polarization measurements.

Discussion

The results show both from pitting corrosion and uniform corrosion that the duplex steel grade has even better corrosion resistance than stainless steel grade type 304L. The PRE values in combination with measured CPT and CCT values also show that from a localized corrosion point of view that the stainless steel grade S32101 provides similar corrosion resistance as steel grade type 316L in neutral environments. There were no results indicating any less corrosion resistance for this stainless steel grade than the standard grades in any environment as previously reported by Clemefña [5]. The most probably reason to this deviation between the two investigations is the variation in the material between the two investigations. In our investigation only pickled rebars were used also noted as received condition and in Clemefña's the rebars were non-pickled and consequently less corrosion resistant.

It cannot be ruled out that the above results are very promising for use of the stainless steel grade S32101 due to the low stable corrosion potential and the high breakdown potential, almost independent of the chloride content. The reproducibility of these measurements shows also that the influence of the amounts of chlorides is less in the alkaline solution compared to a neutral solution. Most useful is the results from the combination of the polarization measurements with measurements of the corrosion potential, since it seems almost impossible to initiate localized corrosion, i.e. pitting corrosion in this alkaline environment. It can also be noticed that a concrete matrix also ages and that the alkalinity is by this procedure going toward more neutral environment. However, this process has to be studied under real conditions where the rebar is cast in concrete. Furthermore, there are results presented recently from at least one field study reported where stainless steels of type 304L, 316L and UNS S32101 were cast in partly and tested in marine atmosphere on a bridge over brackish sea (Ölandsbron) [3]. These results show no corrosion on any of these steel grades and thereby also promising results for the use of stainless steels as rebar materials in concrete. The reference materials type 316L used in our investigation is also in agreement with the stainless steel used in this field study performed by the Swedish Corrosion Institute [3]. However, other steel grades can also be chosen for rebars such as: the stainless steel austenitic of types 304, 304 N, 316LN and duplex stainless steel S32205 for their strength and durability.

It is also important to make measurements on real rebars in stainless steels as in this investigation since the production methods provide different surfaces and surface structure on rebars compared to plate material. It can also be seen from the CPT measurements in this investigation that the resistance to pitting corrosion was slightly lower compared to a plate material. However, the electrochemical polarization measurements in combination with the measurements of the corrosion potential show that rebar of S32101 was resistant to corrosion in these kinds of environments. A previously reported inspection from a 60-year old concrete pier, constructed with stainless steel reinforcing bars (rebar) and exposed to a tropical marine environment showed good performance during its service life, However, a visual inspection showed some signs of corrosion due to insufficient concrete cover. SCC was also identified on bended parts of end hooks of steel grade 3046. From this investigation low corrosion potentials were reported.

Common methods to measure corrosion attacks on rebars in concrete is to follow the corrosion potential or current response with exposure time. However, these methods have previously been used for carbon steels and can only be used on stainless steels in combination with polarization measurements. Any quantitative measurement of the current during a corrosion attack should take into account that stainless steel provides a very large cathodic surface area by the remaining passive protective film during a localized attack that has to be balanced by the current from a minor anodic surface area. Any measurements of a high current in a localized attack might, however, be the result of a minor surface attack on a stainless steel surface, which complicates any calculation of a corrosion rate. A corrosion attack can also accompanied by a change in the corrosion

potential, to a more negative value than for a passive stainless steel, as for example in strong acids. But, according to our measurements in an alkaline environment an active area for corrosion on stainless steels are not even indicated at lower potentials. However, it cannot be excluded that continuous corrosion might occur if the potential for breakdown of the passive film is exceeded in a very strong oxidative environment.

Commonly the influences of crevices when performing electrochemical tests for localized corrosion, such as pitting and crevice corrosion, demands a test cell without crevice influences. For measurements of the outer envelope surfaces of rebars the flush port cell, Avesta cell was not possible to use and a new method was adopted, using a hydrophobic silicon to mask both the end of the rebar and to avoid influence from the edges of the rebar. The results showed when exceeding the breakdown potential that initiation of corrosion was located in the vicinity of the silicon and the corrosion propagated below the silicon as crevice corrosion. However, the corrosion seemed to have started as pitting corrosion probably due to edge effects from the silicon and phase boundary of the steel surface and the results should be interpreted as pitting corrosion rather than crevice corrosion. Nevertheless, if the corrosion started as crevice corrosion the results shows that pitting corrosion in pore-solutions is even harder to initiate than interpreted in this work.

Ericsson et al has also previously pointed out the mechanical properties for S321017. For example, the authors showed for a digester construction, where strength can be utilized to its full extent from a technical point of view, a potential weight saving up to approximately 40% is possible when replacing 304L with S32101.

Conclusions

The duplex steel grade S32101 provides a good corrosion resistance, at least equal or better than that of steel grade 304L against uniform corrosion, stress corrosion cracking, intergranular corrosion and localized corrosion such as pitting and crevice corrosion.

The results demonstrate that no corrosion occurred spontaneously on the stainless steel grade S32101 immersed in pore solutions containing between 1– 42 g/L of chlorides.

Continuous measurements of the corrosion potential show that after 250 hours the reducing environment from the alkaline solution provides very low corrosion potentials, far from any risk of pitting or crevice corrosion, even though the chloride amounts were very high.

The duplex steel grade S32101 shows promising results and good potential as a material for use as rebars in concrete both from a mechanical strength and a corrosion resistance point of view.

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References

1. Wioleta A. Pyc, Performance evaluation of epoxy coated reinforcing steel and corrosion inhibitors in a simulated concrete pore water solution, Masters Thesis, Virginia Polytechnic institute and State University, 1997.
2. S. Wang, R.C Newman, Crevice corrosion of type 316L stainless steel in alkaline chloride solutions, Corrosion, May 2004, pp 448, NACE International, 2004.
3. B. Sederholm, J. Almqvist, Galvanic corrosion of railing posts on concrete bridges-survey of damage and preventive measures, KI Rapport 2003:10E, Swedish Corrosion Institute, Stockholm, Sweden, 2003.
4. Outokumpu Stainless Corrosion Handbook, ninth edition, 2004.
5. G.G. Clemeña, Intermediate report: VTRC 04-R7, Investigation of the resistance of several new metallic reinforcing bars to chloride induced corrosion in concrete, Virginia Transportation Research Council, Charlottesville, 2004.
6. P Castro-Borges, O. Troçonis de Rincon, E. I. Moreno, A. A. Torres Acosta, M Martinez-Madrid, A. Knudsen, Performance of a 60-year-old concrete pier with stainless steel reinforcement, Materials Performance, pp 50 – 55, October 2002.
7. C. Ericsson, V. Jägerström, J. Olsson, S32101 – A New Leaner Duplex Stainless Steel for Tanks and Pressure Vessels, Proceedings 11th Symposium on Corrosion in the Pulp- and Paper Industry, June 7–11, Charleston, South Carolina, 2004.

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