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Accelerated SCC Testing of Stainless Steels According to Corrosion Resistance Classes

M. Borchert[1,†], G. Mori[1], M. Bischof[2], and A. Tomandl[2]

[1]General Analytical and Physical Chemistry, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria
[2]Hilti Corporation, Feldkircherstrasse 100, 9494 Schaan, Liechtenstein

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The German Guidelines for stainless steel in buildings (Z.30.3-6) issued by the German Institute for Building Technology (DIBt) categorizevarious stainless steel grades into five corrosion resistance classes (CRCs). Only 21 frequently used grades are approved and assigned to these CRCs. To assign new or less commonly used materials, a large program of outdoor exposure tests and laboratory tests is required. The present paper shows theresults of stress corrosion cracking (SCC) tests that can distinguish between different CRCs. Slow strain rate tests (SSRT) were performedin various media and at different temperatures. CRC IV could be distinguished from CRC II and CRC III with a 31.3 % Cl^- as $MgCl_2$ solutionat 140 °C. CRC II and CRC III could be differentiated by testing in a 30% Cl^- as $MgCl_2$ solutionat 100 °C.

Keywords : *corrosion resistance class, stress corrosion cracking, stainless steel*

1. Introduction

The German Institute for Building Technology (DIBt) provides a guideline for the correct use of stainless steels in the construction industry[1)]. Therein, the resistance of different materials in various environments is stated. 21 frequently used grades have been grouped in five Corrosion Resistant Classes (CRCs) as shown in Table 1. A fast classification in the different CRCs can be conducted on the basis of PREN, the Pitting Resistant Equivalent Number (Fig. 1). The higher the PREN, the more resistant the material is against pitting corrosion. The PREN gives a first idea about the ability of a material to withstand localized corrosion attack by pitting and crevice corrosion. PREN takes chemical composition of the alloy according to equation (1) into account.

$$\text{PREN} = \%\,\text{Cr} + 3.3 \cdot \%\,\text{Mo} + 16 \cdot \%\,\text{N} \qquad (1)$$

The PREN of CRC I range from 10 to 18, CRC II from 17 to 21, CRC III from 23 to 28 (except 1.4662 which has a PREN of 38), CRC IV from 31 to 40 and CRC V from 42 to 52.

Until now there is no fast classification concerning the resistance to stress corrosion cracking. Stainless steels will suffer from chloride induced stress corrosion cracking (CISCC) under critical environmental and loading conditions. Ambient conditions such as chloride concentration, temperature, pH-value, cation species, pressure and time are strongly influencing CISCC. In addition alloying and metallurgical factors play an important role as well[2-7)].

In case of high strength stainless steels the risk of hydrogen induced stress corrosion cracking (HISCC) is a field of attention. The German guideline for stainless steels in buildings makes no difference between various degrees of cold working, despite the well-known influence of work-hardening on HISCC[8,9)].

In Fig. 2 the resistance to pitting is illustrated as func-

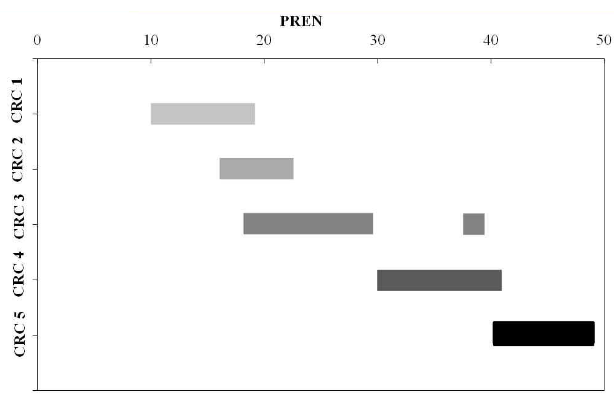


Fig. 1. Range of PREN of stainless steels in different CRCs according to German guideline for stainless steels in buildings (Z-30.3-6).

† Corresponding author: marlies.borchert@unileoben.ac.at

Table 1. Range of corrosion resistance classes according to German guideline for stainless steels in buildings (Z-30.3-6))

CRC [1)]	Short name [2)]	EN [2)]	UNS[3)]	Micro structure	Chemical composition % by wt. Typical values								PREN [4)]
					C	Si	Mn	Cr	Ni	Mo	Cu	others	
I / little	X2CrNi12	1.4003	S41003	Ferrite	≤ 0.03	≤ 1	≤ 1.5	10.5-12.5	0.3-1	−	−	N≤ 0.03	10.5-13.0
	X6Cr17	1.4016		Ferrite	≤ 0.08	≤ 1	≤ 1	16.0-18.0	−	−	−	−	16-18
II / moderate	X5CrNi18-10	1.4301	S30400	Austenite	≤ 0.07	≤ 1	≤ 2	17.0-19.5	8.0-10.5	−	−	N≤ 0.11	17.5-21.3
	X2CrNi18-9	1.4307	S30403	Austenite	≤ 0,03	≤ 1	≤ 2	17.5-19.5	8.0-10.0	−	−	N≤ 0.11	17.5-21.3
	X3CrNiCu18-9-4	1.4567		Austenite	≤ 0.04	≤ 1	≤ 2	17.0-19.0	8.5-10.5	−	3-4	N≤ 0.11	17.0-20.8
	X6CrNiTi18-10	1.4541	S32100	Austenite	≤ 0.08	≤ 1	≤ 2	17.0-19.0	9-12	−	−	Ti(5xC)≤ 0.7	17.0-19.0
	X2CrNiN18-7	1.4318	301LN	Austenite	≤ 0.03	≤ 1	≤ 2	16.5-18.5	6-8	−	−	N0.1-0.2	18.1-21.7
III / medium	X5CrNiMo17-12-2	1.4401	S31600	Austenite	≤ 0.07	≤ 1	≤ 2	16.5-18.5	10-13	2-2.5	−	N≤ 0.11	23.1-28.5
	X2CrNiMo17-12-2	1.4404	S31603	Austenite	≤ 0.03	≤ 1	≤ 2	16.5-18.5	10-13	2-2.5	−	N≤ 0.11	23.1-28.5
	X3CrNiCuMo17-11-3-2	1.4578		Austenite	≤ 0.04	≤ 1	≤ 1	16.5-17.5	10-11	2-2.5	3-3.5	N≤ 0.11	23.1-27.5
	X6CrNiMoTi17-12-2	1.4571	S31635	Austenite	≤ 0.08	≤ 1	≤ 2	16.5-18.5	10.5-13.5	2-2.5	−	(5xC)≤ 0.7	23.1-26.8
	X2CrNiN23-4	1.4362	S32304	Duplex	≤ 0.03	≤ 1	≤ 2	22-24	3.5-5.5	0.1-0.6	0.1-0.6	N0.05-0.2	23.1-19.2
	X2CrNiN22-2	1.4062	S32202	Duplex	0.025	−	1.3	23	2.5	0.3	−	N≤0.2	24.0-27.2
	X2CrMnNiN21-5-1	1.4162	S32101	Duplex	0.03	−	5	21.5	1.5	0.3	−	N0.22	26.0
	X2CrNiMnMoCuN24-4-3-2	1.4662	S82441	Duplex	0.02	−	3	24	6.9	3.1	−	N0.27	38.6
IV / high	X2CrNiMoN17-13-5	1.4439	S31726	Austenite	≤ 0.03	≤ 1	≤ 2	16.5-18.5	12.5-14.5	4-5	−	N0.12-0.22	31.6-38.5
	X2CrNiMoN22-5-3	1.4462	S31803	Duplex	≤ 0.03	≤ 1	≤ 2	21-23	4.5-6.5	2.5-3.5	3.5	N0.1-0.22	30.9-38.1
	X1NiCrMoCu25-20-5	1.4539	N08904	Austenite	≤ 0.02	≤ 0.7	≤ 2	19-21	24-26	4-5	1.2-2	N0.15	34.6-42.9
V / very high	X2CrNiMnMoNbN25-18-5-4	1.4565	S34565	Austenite	≤ 0.03	≤ 1	3.5-6.5	23-26	16-19	3-5	−	Nb≤ 0.15 N0.3-0.6	42.0-52.1
	X1NiCrMoCuN25-20-7	1.4529	N08926	Austenite	≤ 0.02	≤ 0.5	≤ 1	19-21	25	6-7	0.5-1.5	N0.15-0.25	41.2.-48.1
	X1CrNiMoCuN20-18-7	1.4547	S31254	Austenite	≤ 0.02	≤ 0.7	≤ 1	19.5-20.5	17.5-18.5	6-7	0.5-1	N 0.18-0.25	42.2-47.6

1) Corrosion Resistance Class
2) according DIN EN 10088-1:2005-09
3) Unified Numbering System for Metals and Alloys
4) Pitting Resistant Equivalent Number, PREN = % Cr + 3.3 · % Mo + 16 · % N

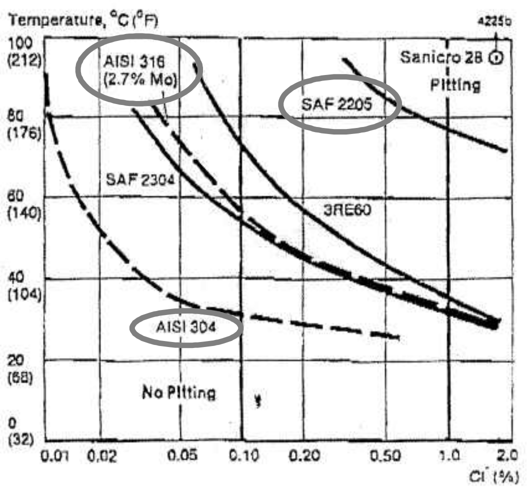


Fig. 2. Resistance to pitting of stainless steels as function of temperature and chloride concentration at a neutral pH[14)].

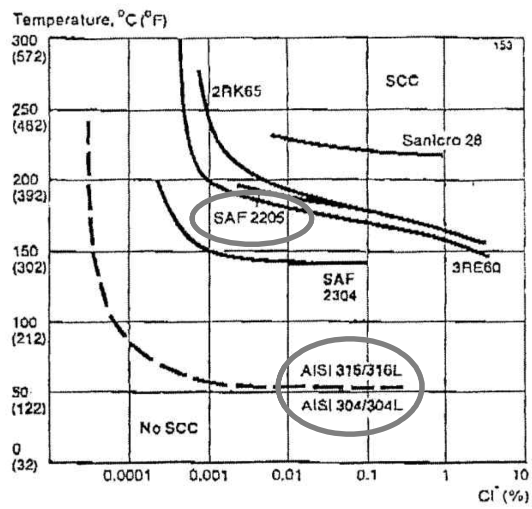


Fig. 3. Resistance to SCC of stainless steels as function of temperature and chloride concentration at a neutral pH[14)].

tion of temperature and chloride concentration at a neutral pH for different alloys. A distinction between stainless steels of CRC II, CRC III and CRC IV can be clearly seen. Thus a clear classification in five CRCs can be done based on the chemical composition and standardized test methods with respect to pitting (STM G48, ASTM G150).

Fig. 3 shows the areas of susceptibility to SCC of stainless steels as function of temperature and chloride concentration at a neutral pH for different alloys. In this diagram 1.4301 (304) and 1.4404 (316) are ranged at the same critical stress level.

The aim of the present work is to identify test conditions to rank different CRCs. In the present work only the CISCC will be investigated.

Table 2. Investigated materials

CRC [1]	Short name [2]	EN [2]	UNS[3]	Micro structure	Chemical composition % by wt. measured values								PREN [4]
					C	Si	Mn	Cr	Ni	Mo	Cu	others	
II	X5CrNi18-10	1.4301	S30403	Austenite	0.025	0.4	1.6	18.2	8.1	0.4	0.6	N0.1	20.6
III	X2CrNiMo17-12-2	1.4404	S31603	Austenite	0.012	0.1	1.1	17.2	11.1	2.0	0.4	N0.1	24.3
IV	X2CrNiMoN22-5-3	1.4462	S31803	Duplex	0.030	1.0	2.0	22.0	5.5	3.0	3.5	N0.1	33.5

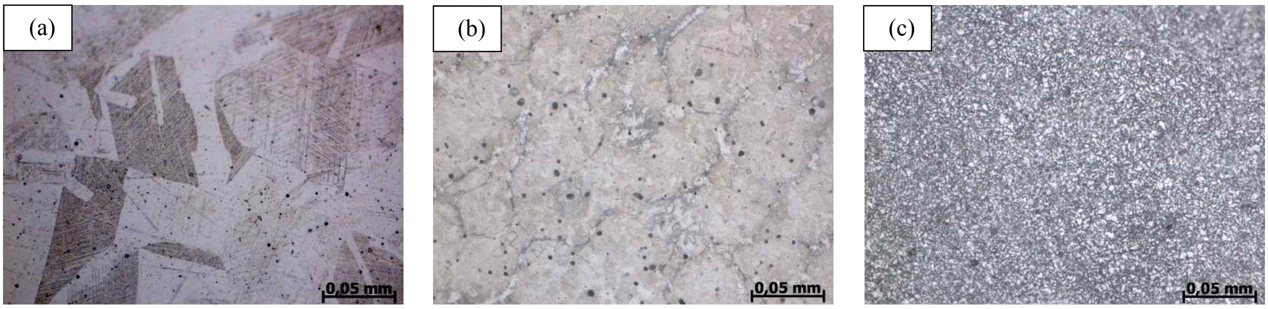


Fig. 4. Microstructure of investigated stainless steels; (a) 1.4301, (b) 1.4404 and (c) 1.4462, etched with V2A pickling solution.

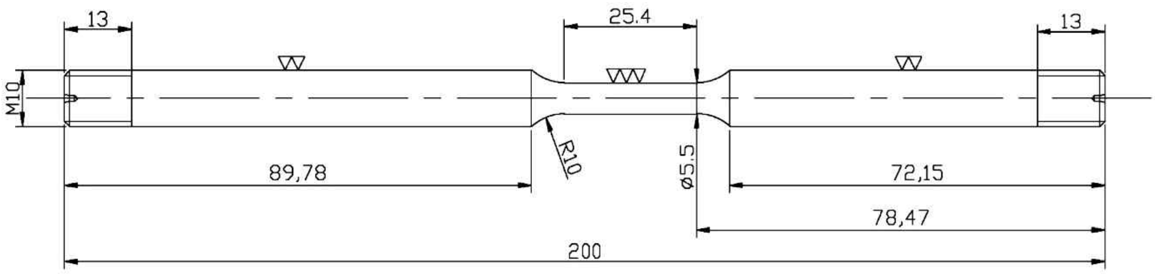


Fig. 5. Geometry of specimen for SSRT.

2. Materials

The chemical compositions of the investigated alloys are shown in Table 2. The 1.4301 is an austenitic stainless steel classified into CRC II. From the CRC III, grade 1.4404 was investigated, which also has an austenitic microstructure. The third material is the duplex steel 1.4462 classified into CRC IV.

The specimens were etched with hot V2A pickling solution. The microstructure is shown in Fig. 4(a-c). Fig. 4(a) shows the austenitic microstructure of 1.4301 with an average grain size of 100 μm. The microstructure of 1.4404 can be seen in Fig. 4b. Its austenite grain size averages 50 μm. The microstructure of duplex stainless steel 1.4462 with a mean grain size of 10 μm is illustrated in Fig. 4(c).

The mechanical properties of all three investigated stainless steels are listed in Table 3. The tensile tests were performed in air at room temperature using a slow strain rate tensile testing machine. Steel 1.4462 was tested in cold worked conditions so the yield and the tensile strength are more than twice as high as the strength values of the materials 1.4301 and 1.4404.

Table 3. Mechanical properties of investigated materials at 25 °C

Alloy	Yield Strength YS [MPa]	Tensile Strength UTS [MPa]	Fracture Elongation ε_f[%]	Reduction of Area RA [%]
1.4301	492	679	56	56
1.4404	517	711	50	54
1.4462	1444	1486	8.4	37

3. Experimental

Raw material was provided as rods with a diameter of 12 mm for the 1.4301 and 1.4404 and as a wire with a diameter of 6 mm for the 1.4462. The rods were solution annealed and the wire was cold formed.

SSRTs were conducted on tensile specimens with a final gauge diameter of 4.8 mm and a gauge length of 25 mm for 1.4301 and 1.4404 and a final gauge diameter of 2.8 mm and a gauge length of 15 mm for 1.4462. The exact geometry of specimens is shown in Fig. 5[10]. All specimens were electropolished prior to testing, using a

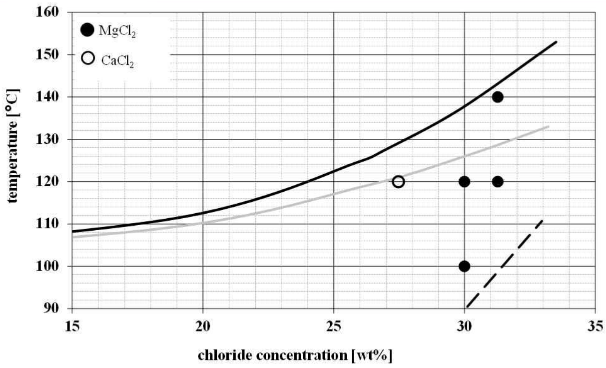


Fig. 6. Investigated test conditions in the measurement window for aqueous $CaCl_2$ and $MgCl_2$ solutions.

Table 4. Chloride concentration and chemical composition of test solution

chloride concentration [wt.%]	salt concentration	composition of test solution
27.5	43 % $CaCl_2$	57 g $CaCl_2 \cdot 2\ H_2O$ 43 ml H_2O
30	40.3 % $MgCl_2$	86 g $MgCl_2 \cdot 6H_2O$ 14 ml H_2O
31.3	42 % $MgCl_2$	90 g $MgCl_2 \cdot 6H_2O$ 10 ml H_2O

commercial H_2SO_4-H_3PO_4 electrolyte E 268 A from Poligrat ™. Thereby residual stresses due to sample preparation (caused by machining) were removed[11]. Afterwards the specimens were degreased with ethanol in an ultrasonic bath and washed with deionized H_2O. Subsequent to this pretreatment all samples were stored for 24 h in a desiccator to form a natural protective oxide film, which is typical for stainless steels. Consequently, all samples were subject to the same conditions for the formation of the passive film.

The SSRTs were done at a strain rate of 10^{-5} s^{-1}. Specimens were put in double-walled glass cylinders (300 ml volume) filled with the test solutions.

During the tests both load and elongation were measured continuously. The recorded data was converted to stress- strain curves for each specimen. The stress-strain curves in the investigated chloride solutions were compared to the results obtained in glycerine at the according temperature.

The controlled variations of electrolyte parameters like chloride content and temperature in order to investigate their specific influences are shown in Fig. 6[12]. The parameters had been varied, until a combination was found which made the difference between the CRCs visible.

Optical microscopy was used to determine qualitative crack densities and degree of corrosion attack on specimens.

4. Results

In Fig. 6 the investigated test conditions are presented. The test solutions were electrolytes containing either $MgCl_2$ (full circles) or $CaCl_2$ (empty circle) with different chloride concentrations at various temperatures. Measuring the exact pH value in such hot and concentrated salt solutions is very difficult, but first approaches by Speidel[5] showed that $MgCl_2$ solutions do have a lower pH than $CaCl_2$ solutions at similar concentrations. Figure 6 assigns the boiling temperature curves of aqueous solutions of $MgCl_2$ (black curve) and of $CaCl_2$ (grey curve). The black dashed line marks the crystallization temperature of the $MgCl_2$ solution. To avoid any crystallization of $MgCl_2$ at low temperatures the chloride concentration was reduced from 31.3 % Cl^- to 30 % Cl^-. In Table 4 chloride concentrations and chemical compositions of test solutions are given. Furthermore the proportions of distilled H_2O and salt are specified.

The stress strain curves of the SSRTs are shown in Fig. 7. For the purpose of a better comparison the susceptibility index (SI) was calculated[13].

$$SI = 100 \cdot (1 - (\frac{\text{property}_{\text{aggresiv}}}{\text{proberty}_{\text{inert}}})) \tag{2}$$

Parameters: tensile strength, yield strength, fracture elongation and fracture energy (equal to $\int \sigma d\varepsilon$)

In the present paper the fracture elongation was used as parameter for the SI-calculation. In Table 5 the SI-values of all tests are summarized. The detailed results of the conducted SSRTs can be seen in Fig. 7, where the dashed lines represent the behavior of the alloys in the aggressive solution and the solid lines show the behavior of the alloys in the inert solution.

The tests conducted in the $MgCl_2$ solution with 31.3 % Cl^- at 140 °C result in the highest differences between the different CRCs. While CRC IV can be identified with a SI of 29.2, the SI of CRC III amounts to 68.9 and CRC II shows a SI of 77.2, and thus the corrosive attack is more severe.

In the $CaCl_2$ solution with a Cl^- content of 27.5 % at 120 °C, the steel 1.4404 shows a SI of 0 thus no SCC occurs. Since 1.4301 has a SI of only 12.5, no sufficient distinction between CRC III and CRC II can be made. As illustrated in Fig. 7 the stress strain curves of the speci-

Table 5. Susceptibility index of 1.4301, 1.4404 and 1.4462 in investigated test solutions

T [°C]	CRC	Alloy	Susceptibility Index of different chloride concentrations		
			27.5 % Cl^- as $CaCl_2$	30 % Cl^- as $MgCl_2$	31.3 % Cl^- as $MgCl_2$
140	IV	1.4462			29.2
	III	1.4404			68.9
	II	1.4301			77.2
120	IV	1.4462			
	III	1.4404	00.0	57.6	51.6
	II	1.4301	12.5	67.2	50.0
100	IV	1.4462			
	III	1.4404		43.5	
	II	1.4301		51.2	

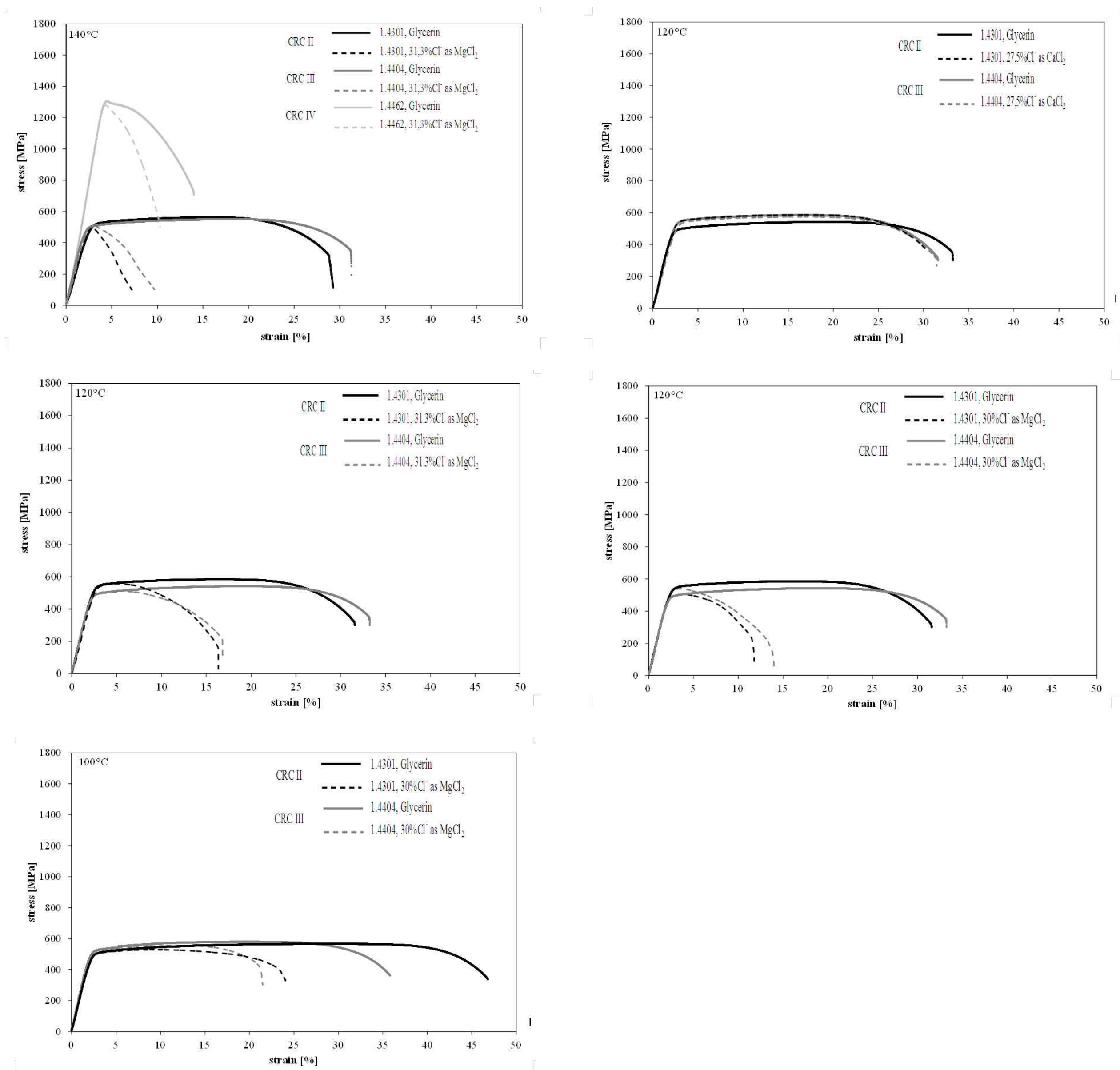


Fig. 7. SSRTs of the stainless steels 1.4301, 1.4404 and 1.4462 in aqueous chloride solutions at s strain rate of 10^{-5} s^{-1}.

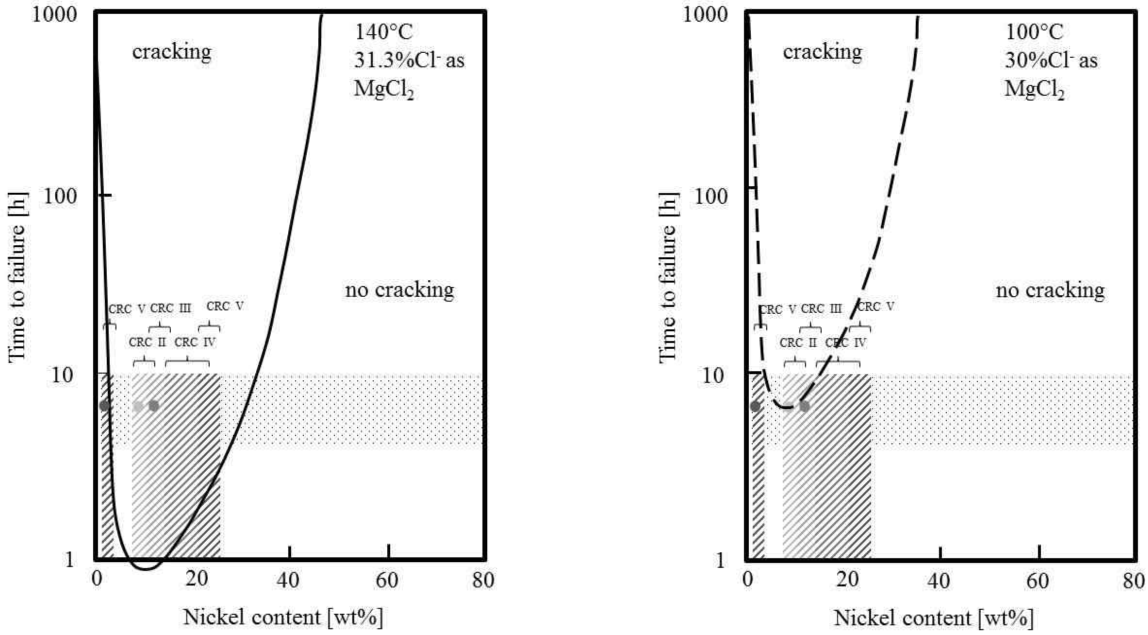
Fig. 8. Surface attack and crack density of SSRT specimens in different test solutions.

mens in this aggressive solution and those in inert solution are almost identical.

The results of the SSRTs in the $MgCl_2$ solution with 31.3 % Cl^- at 120 °C show that under these conditions a clear distinction between CRC III and CRC II is not possible as well. Steel 1.4404 shows a SI of 51.6, while steel 1.4301 has a SI of 50.0 so the damage by SCC is almost equal for both alloys (see Table 5 and Fig. 7).

A distinction between CRC III and CRC II neither can be seen by reducing the chloride content to 30 % Cl^- in a $MgCl_2$-solution at 120 °C. However when tested in the same $MgCl_2$ solution (30 % Cl^-) but at a reduced temperature of 100 °C there is a small difference between the results of CRC III and CRC II. To quantify this fact, steel 1.4404 shows a SI of 43.5 and steel 1.4301 shows a SI of 50.0 (see Table 5 and Fig. 7).

Fig. 8 shows some of the broken specimens. For samples tested in glycerine, only the results at 120 °C are shown since there was no significant difference to the specimens tested at other temperatures. A strong reduction of area can be observed in all specimens tested in glycerine as well as in $CaCl_2$-solution with 27.5 % Cl^-. Specimens of steel 1.4404 tested in $MgCl_2$-solution with 31.3 % Cl^- at 140 °C and at 120 °C exhibits severe SCC attack. Material 1.4404, in 30 % Cl- solution at 120 °C and 100 °C, shows only a low susceptibility to SCC (illustrated in Fig. 8 and Table 5). Material 1.4301 exhibits a severe SCC attack in all tested solutions, characterized by high number of cracks and brittle fractures (Fig. 8). Steel 1.4404 is more resistant to SCC in the chosen environments than steel 1.4301. Under more aggressive conditions (higher chloride content and/or higher temperature) both materials show severe SCC.



(a) (b)

Fig. 9. (a) Time to failure dependent on the Nickel content (Copson Curve[4]) (b) Copson Curve at a lower temperature, ● 1.4301, ● 1.4404, ●1.4462.

5. Discussion

As shown in Figure 1 all approved grades from the German guideline of stainless steels in buildings can be grouped in five CRCs considering their PREN, although the PREN ranges overlap to a certain extent.

A distinction regarding the susceptibility to SCC between CRC IV and lower CRCs is obtained in the $MgCl_2$ solution with 31.3 % Cl^- at 140 °C. As a consequence of the high strength of material 1.4462 the susceptibility to SCC should also be very high; however this material shows the best resistance to SCC of all tested materials, due to its duplex microstructure. Yet between CRC III and CRC II a distinction is difficult because of similar properties (Table 2 and Table 3). In Fig. 9(a) the Copson Curve is shown (black curve)[4]. This curve shows the limit of SCC formation of austenitic steels in 31.3 % Cl^- as $MgCl_2$ at 140 °C as function of testing time and Nickel content of the alloy. The horizontal doted range shows the time window of the SSRT in this paper. The vertical hatched ranges show the Nickel content of the different CRCs, which sometimes overlap. The grey dots in Fig 9 symbolize the investigated materials. The investigated duplex stainless steel is outside the area of cracking. The two other dots are right in the middle of the cracking zone due to their Nickel content. This suits with the results shown in Table 5.

The dashed line in Fig. 9(b) shows the Copson Curve shifted according to Arrhenius equation when reducing the temperature by 40 °C (equal to a time shift factor of ca. 2^4). The slope of the curve in the range of 8 - 13 wt. % Nickel is very small so there is a no sharp transition from cracking to no cracking at a given temperature. It can be seen, that the 1.4301 and the 1.4404 (grey dots) are close to the minimum of the curve. Both dots are close to the line between cracking and no cracking. So consequently no sharp distinction between CRC III and CRC II could be found.

In this paper the fracture elongation as SI parameter is also used as an assessment criterion. As could be seen in Table 5, a certain distinction between CRC III and CRC II can be achieved.

6. Conclusions

SSRT have proven to be suitable for the distinction of stainless steel grades from different CRCs and can be used for further measurements of other grades as well as various degrees of cold working.

On the basis of PREN the five CRCs can be distinguished, hence each CRC is assigned a certain PREN range. SSRTs were conducted in various media. In the $MgCl_2$ solution with 31.3 % Cl^- at 140 °C a distinction between CRC IV and CRC III+II could be seen using the fracture elongation as parameter. Also a (less pronounced) distinction can be found for CRC III and CRC

II in the $MgCl_2$ solution with 30 % Cl^- at 100 °C especially when considering the SI.

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