

THE INFLUENCE OF THE SURFACE FINISHING ON THE ELECTROCHEMICAL BEHAVIOUR OF DIN 1.4404 AND DIN 1.4410 STEELS

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Abstract

It is well known that the breakdown potential (E_b) and the open circuit potential (E_{ocp}) are important parameters to evaluate the resistance of metallic materials against corrosion. Nevertheless, the literature presents scattered values of these parameters for stainless steels (SS). Many factors may contribute to this dispersion of published E_b and E_{ocp} values. It has been proposed that the finishing and/or final treatment of the surface is one of those factors.

To address this question, the influence of the surface finishing on the average roughness (R_a), residual stress (τ) and electrochemical behaviour of DIN 1.4404 and DIN 1.4410 steels have been considered. Samples from both steels were prepared with different finishing degrees with SiC paper. Roughness, residual stress and electrochemical tests were performed on samples with various surface finishing. Electrochemical studies were conducted in an Avesta cell and steel electrodes immersed in 1 M NaCl or 0.5 M MgCl₂ aqueous solutions.

We found that when steels are immersed in sodium chloride or magnesium chloride aqueous solutions there is no significant change in the variation of the E_{ocp} and E_b values as the average roughness increases and therefore we can conclude that these parameters are not affected by the final treatment or by the solution composition.

Keywords: DIN 1.4404, DIN 1.4410, Surface Finishing, Electrochemical Parameters

Influência do Acabamento Superficial no Comportamento Electroquímico dos Aços DIN 1.4404 e DIN 1.4410

Resumo

É do conhecimento geral que os valores do potencial de ruptura da passivação (E_b) e do potencial em circuito aberto (E_{ocp}) são parâmetros importantes para avaliar a resistência à corrosão dos materiais metálicos. Contudo, pelo menos no que se refere a aços inoxidáveis a literatura apresenta resultados muito divergentes. Vários factores poderão contribuir para a referida diversidade de valores, entre eles, o acabamento ou tratamento final da superfície.

Este estudo pretende avaliar a influência do acabamento superficial na rugosidade média (R_a), tensão residual (τ) e resposta electroquímica dos aços em estudo.

De modo a serem atingidos os objectivos foram preparadas amostras de ambos os aços com diferentes acabamentos com lixas de SiC, sendo efectuadas medidas de rugosidade, de tensão residual e realizados ensaios electroquímicos de polarização potenciodinâmica. Os ensaios electroquímicos foram realizados na célula Avesta com amostras de ambos os aços com diferentes acabamentos superficiais, em soluções aquosas de NaCl 1 M e MgCl₂ 0,5 M.

Das medidas efectuadas conclui-se que não há uma variação significativa nos valores de E_{ocp} e E_b com o aumento da rugosidade média para os dois aços em estudo, tanto no meio de cloreto de sódio como no meio de cloreto de magnésio. Pelo que se conclui que o tratamento final e composição da solução, no que se refere ao catião, não afectam significativamente os parâmetros electroquímicos.

Palavras Chave: DIN 1.4404, DIN 1.4410, Acabamento Superficial, Parâmetros Electroquímicos

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1. INTRODUCTION

Stainless steels are selected as engineering materials due to their excellent resistance to corrosion when immersed in various media. Their resistance is due to the presence of a thin metal oxide layer covering the steel surface (known as the passive film), typically 1 to 3 nm thick. The presence of certain anions adsorbed on the surface can be detrimental to the film stability and lead to pit initiation [1].

The austenitic stainless steel (DIN 1.4404) presents good corrosion resistance in many media. The duplex (austenitic-ferritic) steel (DIN 1.4410) combines high strength; good toughness and very good corrosion resistance, especially in relation to stress corrosion cracking and corrosion fatigue [2-4].

The breakdown potential (E_b) and the open circuit potential (E_{ocp}) are important parameters to evaluate the resistance of the materials against corrosion. Nevertheless, the literature presents scattered values of the above-mentioned parameters for the stainless steels in general [5, 6].

The main differences between the two steels that are object of this study reside on the Cr, Ni, N and Cu contents. DIN 1.4410 contains higher percentages of Cr, N and Cu, but lower percentage of Ni. Concerning to the microstructure the DIN 1.4404 presents a pure austenitic microstructure, while DIN 1.4410 has a dual microstructure constituted by austenite and ferrite, in a proportion of typically 60-40%.

SUDES *et al.* [5] have studied the behavior of 316L SS in 1 M NaCl grinded with 600 grit and 1200 grit SiC paper and then polished with alumina powder down to 0.1 µm sizes. They have obtained a pitting potential of +200 mV vs. SCE. REFAEY *et al.* [6] have obtained E_b values around +125 mV vs. Ag/AgCl (aprox. +145mV vs. SCE) for the same material and in 1 M NaCl, after polishing successively with emery papers up to grade 400 grit.

DAWSON *et al.* [7] have obtained a pitting potential value of +200 mV vs. SCE AISI 316 in 0.5 M NaCl after grinding with decreasing SiC grit size from 320 to 1000, polished down to 1µm with alumina and kept overnight in a desiccator.

Due to the large scattering on the electrochemical parameters found in the literature and its influence on other

corrosion phenomena like, e.g. stress corrosion cracking, the surface finishing of the electrodes may be the reason for those discrepancies.

Then we have decided to perform a systematic study on the influence of the surface finishing of both steels, (DIN 1.4404 and DIN 1.4410), on their electrochemical parameters, considering two immersing chloride containing media of identical ionic strength, namely 1 M NaCl and 0.5 M MgCl₂ aqueous solutions.

The pH was measured before and after each test. A Radiometer analytical REF pH C2015-8 electrode, calibrated at pHs 4.7 and 10 was used. Duplicates of cyclic potentiodynamic polarisations and of open circuit potentials were performed in each environment.

The open circuit potential (E_{ocp}) was monitored for 10 minutes and the cyclic potentiodynamic polarisations were performed at 10 mV/minute scan rate (≈ 0.17 mV/s), according to ASTM G61-86 [8] and ASTM F2129-04 [9], in the potential ranges from +300 to 1200 and -200 to 1600 mV vs. SCE, for DIN 1.4404 and DIN 1.4410 stainless steels, respectively.

Surface roughness measurements were performed with a Mitutoyo Surftest 2001 Series 178. Test specimen roughnesses were measured after 24 h of passivation before and after the cyclic potentiodynamic polarisations. For each test specimen, three measurements have been carried out in two perpendicular directions (longitudinal and transversal direction). The roughness measurement after the cyclic potentiodynamic polarisation was performed only on DIN 1.4410 steel samples, since the surface of DIN 1.4404 was quite damaged to allow the roughness measurement. Roughness measurements have been complemented with morphological analysis by optical microscopy and on a FE-SEM, model JEOL 6500 in the secondary electrons mode. Residual stress measurements were performed in two directions (longitudinal and transversal) by XR diffraction using the sin 2ψ method. A RIGAKU Strainflex MSF-2M, using K β radiation of a Cr target, and the (311) diffraction planes of the austenite CFC structure were used [10,11]. Scanning was performed between $5^\circ < \psi < 40^\circ$ in 5 steps. The irradiated

2. EXPERIMENTAL PROCEDURE

2.1. Electrochemical set-up

An Avesta cell was set up with a Pt – Sensortechnik Meinsberg GmbH SE 11 BNC (surface area of 4.9 cm²) as counter electrode (CE), a commercial saturated calomel electrode (SCE) (Radiometer analytical, REF XR110) as reference electrode (RE) and stainless steel DIN 1.4404 or DIN 1.4410 both in the annealed condition (Table 1) samples supplied by Outokumpu as working electrodes (WE), with a surface area of 1 cm².

The WE surfaces were prepared by sequentially wet grinding with SiC papers (Struers) of different grit numbers, washed several times, degreased in acetone, dried and left exposed to air for at least 24h prior to the experiments.

1 M NaCl and 0.5 M MgCl₂ aqueous solutions were prepared using p.a. grade reagents (Fisher Scientific and Panreac) and Milli-Q water (Milipore). The electrochemical measurements were carried out in 1 M NaCl and in 0.5M MgCl₂ aqueous solutions, at a temperature of $27 \pm 1^\circ\text{C}$. The solution was stirred during measurements by bubbling air.

Table 1 - Chemical composition (wt %) of DIN 1.4404 and DIN 1.4410 steels.

Grade	Fe	C	Si	Mn	P	S	Cr	Ni	Mo	N	Cu
DIN 1.4404	Bal.	0.026	0.37	1.11	0.032	0.001	16.6	10.2	2.04	0.025	-
DIN 1.4410	Bal.	0.021	0.39	1.42	0.020	0.001	22.5	5.8	3.16	0.166	0.20

area was about 100 mm². A peak angle of approximately 150° was determined.

3. RESULTS AND DISCUSSION

3.1. Optical observation

Optical microscopy images for the DIN 1.4404 and DIN 1.4410 steels surfaces after grinding with SiC paper grades 80, 120, 220, 320, 500 and 1200 show a gradual decrease in roughness as the grit size number increases but only until the #500. Afterwards, no further significant changes were observed.

Figures 1 and **2** show images of the sample surface obtained after cyclic potentiodynamic polarisation, in 1M NaCl and 0.5M MgCl₂ solutions. The images of DIN 1.4404 after being immersed in the NaCl as compared with those from immersions in the MgCl₂ solution show higher density of pits. However the pits are deeper and wider in the second solution mentioned.

The DIN 1.4410 steel samples immersed in the NaCl solution also present random pits but the test area is not as worn out, while that for samples immersed in the MgCl₂ solution show only general corrosion.

3.2. Roughness

Figure 3 presents the average Ra values for the two steels as a function of SiC grit size used for finishing, starting with a value of order of 0.3 µm and ending up with a value less than 0.1µm. Observation of the grinded surfaces shows that when finishing is performed with lower grit size, the surfaces present deformed metal layers over the surface, although these deformation decreased as grit size increased. These deformations may lead to small crevices when the electrodes are immersed in the electrolyte and therefore may contribute to affect the electrochemical data (see **Figure 4**).

Furthermore the analysis of the data given in **Figure 3** shows that the DIN 1.4410 samples when compared with the corresponding ones from the DIN 1.4404 present, in general, higher roughness values.

This might be eventually justified by differences in hardness presented by the phases: austenite and ferrite.

In fact, microhardness tests performed on both austenite and ferrite grain showed

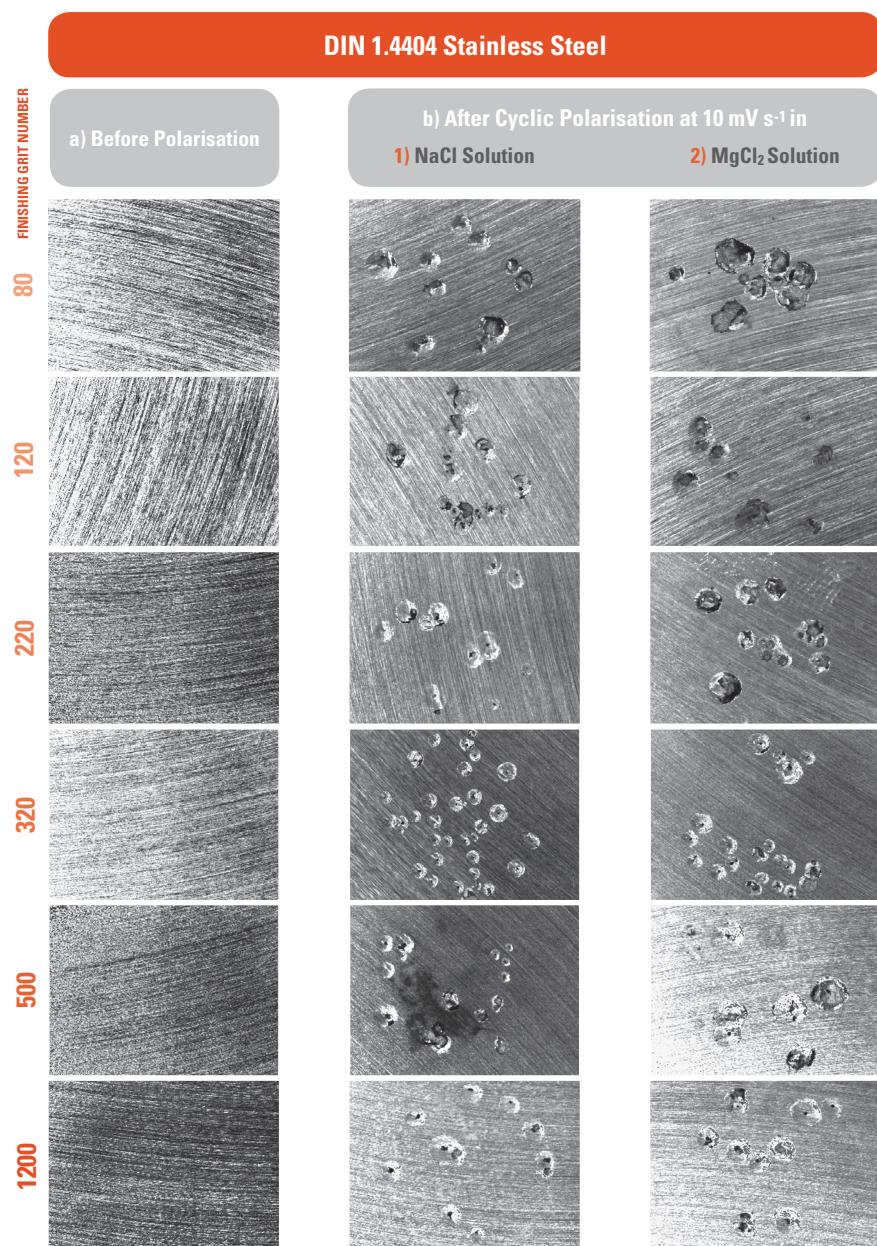


Fig. 1 – Optical images of the DIN 1.4404 SS samples after grinding with SiC of different grit sizes, before polarization (a) or after polarization in NaCl (b₁) and MgCl₂ (b₂) aqueous solutions. Amplification 80X.

that these phase have hardnesses of 329 HV0,015 and 296 HV0,015, respectively (**Figure 5**).

Nevertheless, both steels reach identical roughness values of 0.05 µm, when the finishing is made with grit size #1200.

3.3. Residual stress measurements

Residual stress measurements were performed in order to evaluate the influence of the average roughness on the residual stress (τ), and eventually, correlate

this with the electrochemical data. For the graphical representation, residual stress values obtained in transversal direction for DIN 1.4404 and DIN 1.4410 were chosen but it was concluded that the residual stresses in the longitudinal direction present identical behaviour. Results in **Figure 6** show compression stresses for all the samples, which decrease as the average roughness increases. Residual stress in the transversal direction shows no significant differences for the

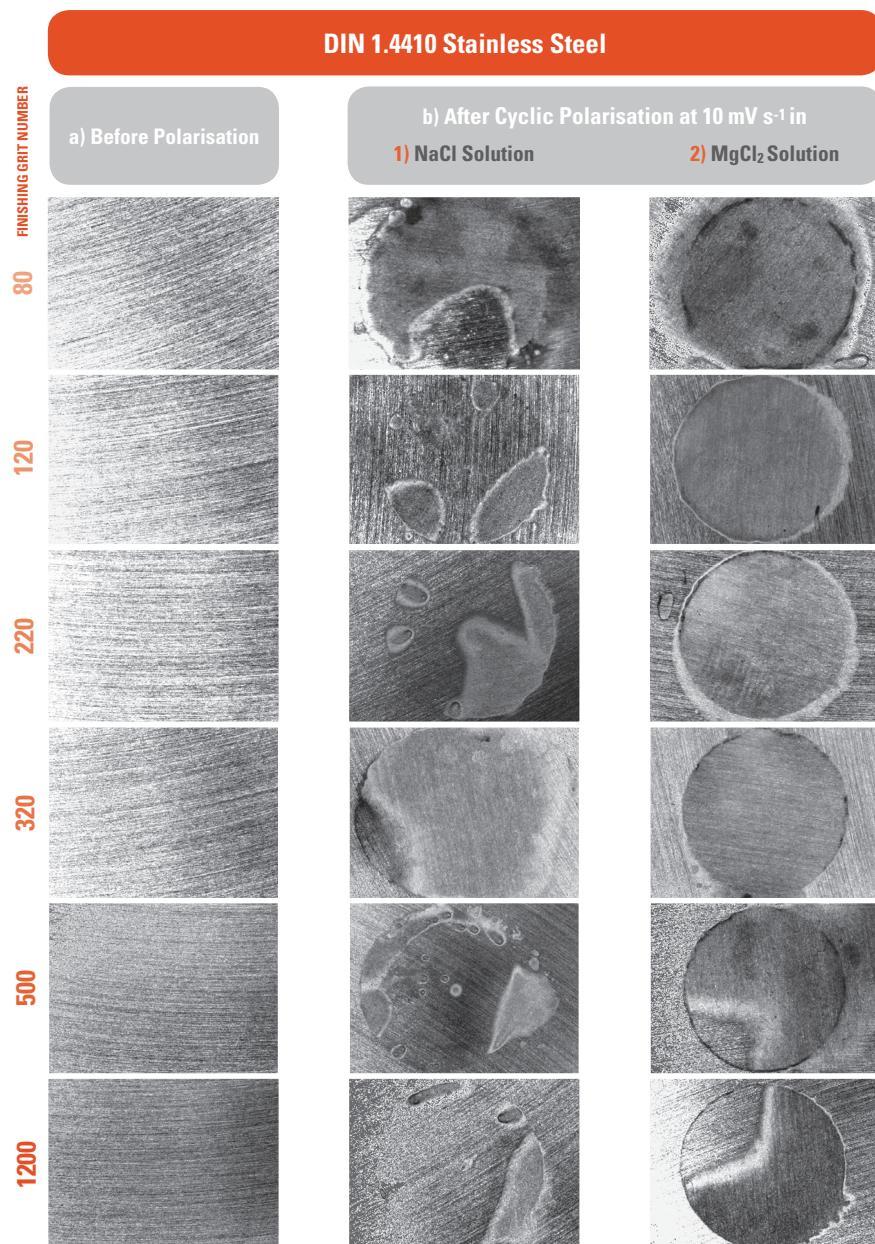


Fig. 2 – Optical images of the DIN 1.4410 steel samples after grinding with SiC of different grit sizes, before polarization (a) or after polarization in NaCl and in (b₁) MgCl₂ (b₂) aqueous solutions. Amplification 80X.

two steels. These compressive stresses contribute to inhibit stress corrosion cracking and make crack nucleation more difficult. Residual stress data do not show differences between the behaviour of the two steel samples.

3.4. Electrochemical data

The influence of the surface finishing of both steels (DIN 1.4404 and DIN 1.4410) on their electrochemical parameters, when immersed in the chloride containing media

of identical ionic strength, namely 1 M NaCl or 0.5 M MgCl₂ aqueous solutions, was investigated in this study.

Table 2 presents the electrochemical parameters obtained from the open circuit potential and cyclic polarisation measurements for both materials in both media. Electrochemical values presented are the average of 2 measurements.

Figures 7 to 12 present the comparison of the open circuit and pitting potentials as function of the average roughness,

for both steels in both media. The E_{ocp} values of the DIN 1.4404 present a slight displacement in the negative direction, as the average roughness increases. A similar behaviour is observed with the DIN 1.4410 samples, although a higher dispersion could be observed for surfaces with lower roughness.

However these differences may not be relevant as, for both media, E_{ocp} values for DIN 1.4404 presents a dispersion of less than 100 mV, while for the DIN 1.4410, this dispersion is slightly higher, 150 mV. These results suggest that there are no significant changes on the E_{ocp} values due to the roughness. The same conclusion can be drawn from the E_b values, within a dispersion of 60-70 mV for both materials although DIN 1.4410 revealed significant differences between both media with higher dispersion for MgCl₂. The E_{ocp} values, referred to the same reference electrode (SCE), for DIN 1.4410 are always positive in both media, while those of the DIN 1.4404 are mostly negative regardless of the surface condition.

The pitting potential values (E_b) of the DIN 1.4404 samples are slightly lower in the MgCl₂ solution and lie typically in a scatter band of 150 mV for MgCl₂ and of 100 mV for NaCl, for all the grit sizes. The DIN 1.4410 samples present a wider scatter range of pitting potential values when compare to the average roughness increases for both media.

4. CONCLUSIONS

Images from optical microscopy show a significant amount of deformed material on the surface depending on the surface finishing degree.

These deformations may lead to small crevices on the electrode surface. Surface preparation operations introduce residual compressive stresses in the range 150 to 300 MPa for DIN 1.4404 and 170 to 330 MPa for DIN 1.4410, a decrease being observed as the grit size increased. Data has also shown that corrosion of the DIN 1.4404 samples occurs in the form of pitting in both media; while that for the DIN 1.4410 occurs in the form of general corrosion. This rather different behaviour may be explained by the differences in the

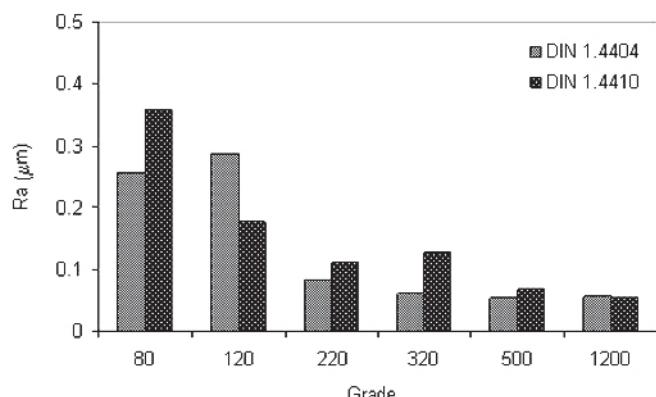


Fig. 3 – Average roughness Ra (average of the roughness obtained in longitudinal and transversal directions, for the DIN1.4404 SS and DIN 1.4410 steel samples as function of surface finishing grit sizes.

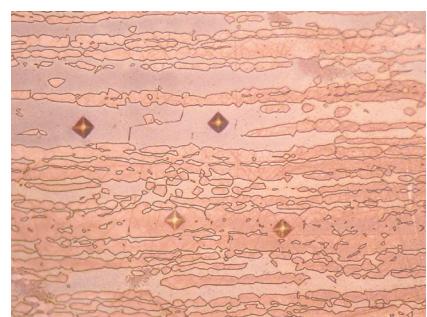


Fig. 5 – Duplex steel microstructure with indentations on austenite and ferrite phases.

chemical composition of the two materials. For DIN 1.4404 no noticeable variation of E_b with compressive surface stress has been observed, while for the DIN 1.4410, somewhat more scattered results have been obtained; although E_b seem also no to be influenced by residual stress.

DIN 1.410 samples presented significantly higher pitting potentials (more positive) as compared with the DIN 1.4404 (~1200 against 400 mV vs SCE). For all the situations considered in this study, the DIN 1.4410 has shown higher corrosion resistance when compared with the DIN 1.4404, under identical surface finishing conditions. This is in fact the expected behaviour considering their chemical composition.

Finally we would like to emphasize that this study has not supplied any significant evidence of the dependence of the electrochemical parameters on the surface finishing degree for the DIN1.4404 and DIN 1.4410 steels in chloride media.

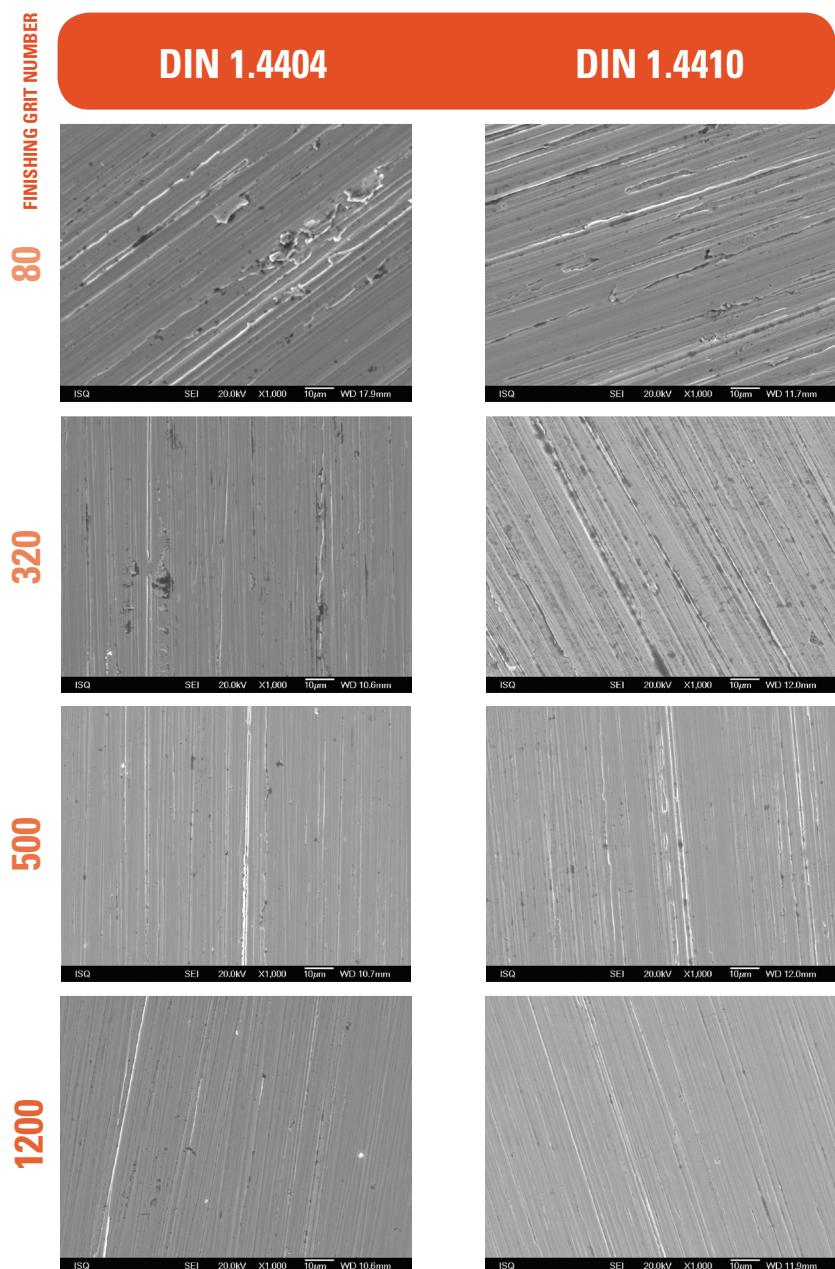


Fig. 4 – SEM microographies of the DIN 1.4404 SS and DIN 1.4410 steel samples as a function of surface finishing grit sizes. Amplification 1000x.

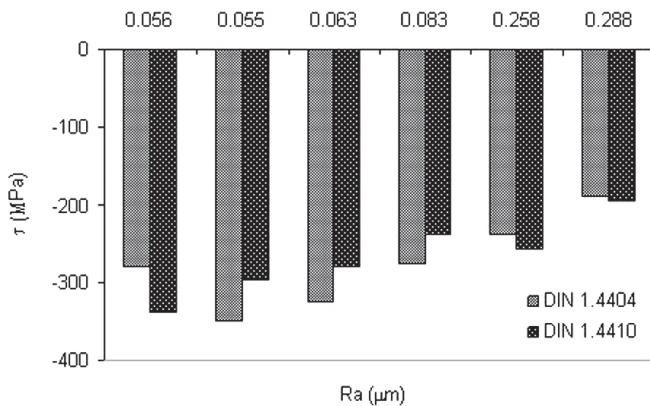


Fig. 6 – Residual stress values (in the transversal direction) of the DIN 1.4404 SS and DIN 1.4410 steel samples as function of the average roughness (average of the roughness obtained in longitudinal and transversal directions).

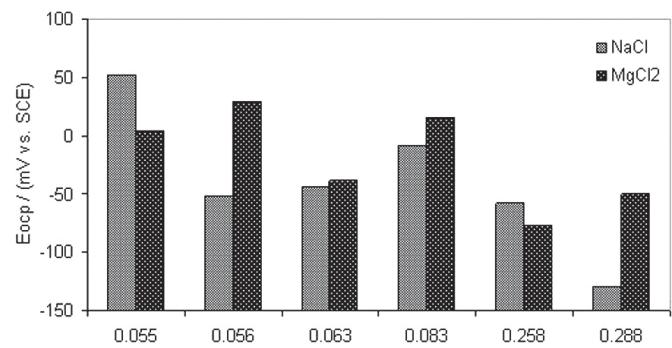


Fig. 7 – Open circuit potential of the DIN 1.4404 SS samples, in both chloride media, as function of the roughness, R_a (average of the roughness obtained in longitudinal and transversal directions).

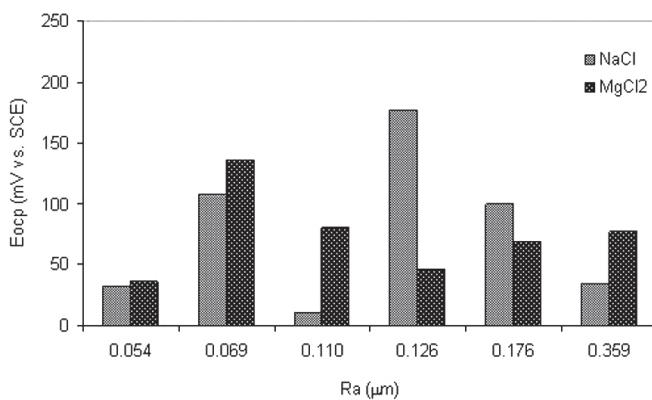


Fig. 8 – Open circuit potential of the DIN 1.4410 steel samples in both chloride media, as function of the roughness, R_a (average of the roughness obtained in longitudinal and transversal directions).

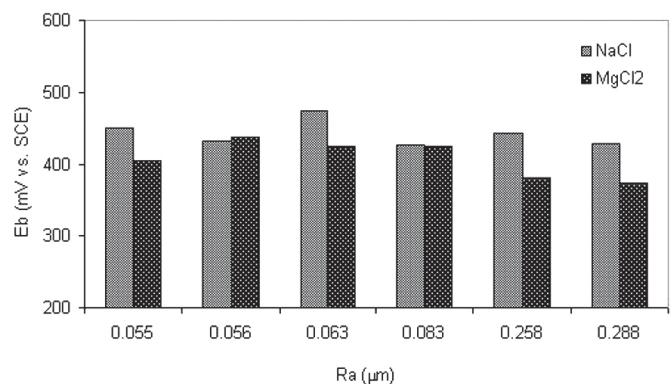


Fig. 9 – Pitting potential of the 1.4404 SS samples, in both chloride media, as function of the roughness, R_a (average of the roughness obtained in longitudinal and transversal directions).

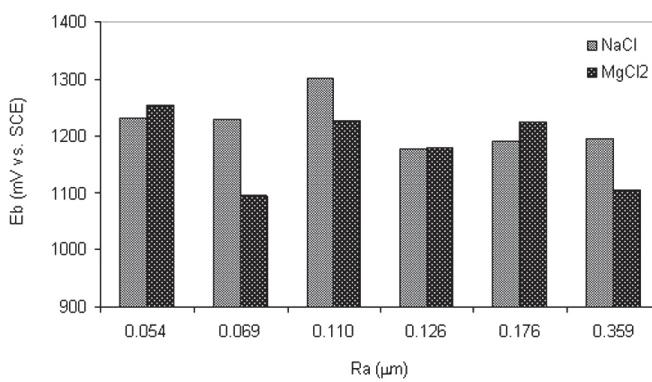


Fig. 10 – Pitting potential of the DIN 1.4410 steel samples, in both chloride media, as function of the roughness, R_a (average of the roughness obtained in longitudinal and transversal directions).

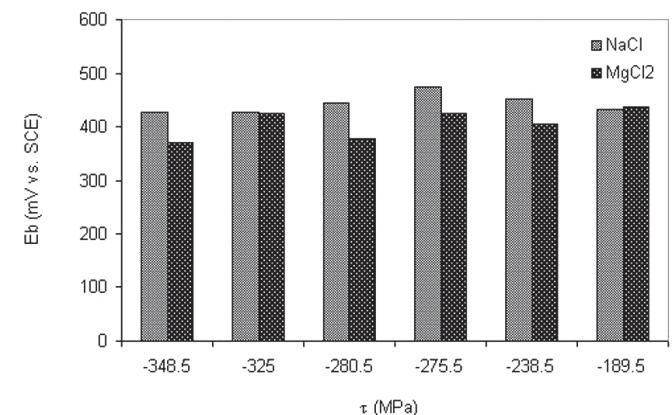


Fig. 11 – Pitting potential of the DIN 1.4404 SS samples, in both chloride media, as function of the residual stress in the transversal direction, τ .

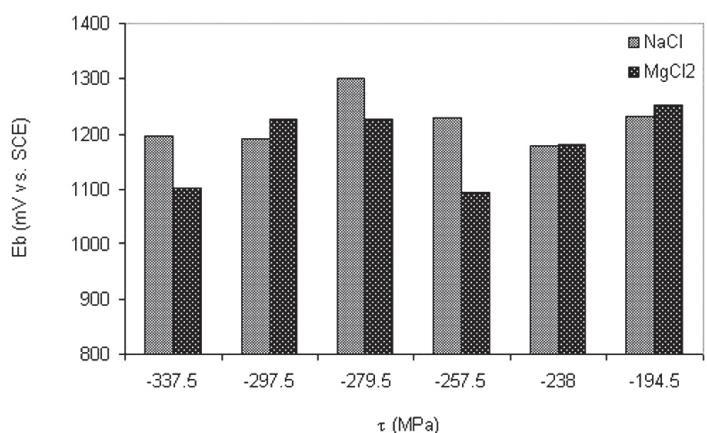


Fig. 12 – Pitting potential of the DIN 1.4410 steel samples, in both chloride media, as function of the residual stress in the transversal direction, τ .

Table 2 - Corrosion parameters of the DIN 1.4404 and DIN 1.4410 samples.

Electrolyte	Grit size number	Open circuit potential		Cyclic potentiodynamic polarisation			
		E _{ocp} (mV vs. SCE)		E _{zc} (mV vs. SCE)		E _b (mV vs. SCE)	
		DIN 1.4404	DIN 1.4410	DIN 1.4404	DIN 1.4410	DIN 1.4404	DIN 1.4410
1 M NaCl	80	-58.5	34.1	-102.7	-142.9	444.0	1196.6
	120	-130.0	99.3	-156.9	-105.2	428.6	1190.5
	220	-7.5	10.2	-103.1	-118.1	427.8	1301.1
	320	-44.5	176.7	-112.2	-32.6	473.8	1177.6
	500	52.0	107.3	-84.9	-82.2	451.5	1230.1
	1200	-52.8	32.5	-180.6	-95.6	433.6	1232.6
0.5 M MgCl ₂	80	-77.0	77.6	-124.0	-82.9	379.9	1103.6
	120	-50.5	69.2	-120.3	-124.1	372.2	1226.1
	220	16.0	80.8	-114.2	-128.5	425.9	1228.1
	320	-39.0	45.8	-175.5	-81.7	425.7	1180.8
	500	-4.5	136.7	-147.9	-64.8	405.6	1095.7
	1200	30.0	36.5	-141.1	-124.2	438.5	1253.7

E_{ocp} – Open Circuit Potential; E_{zc} – Zero Current Potential; E_b – Breakdown or Critical Pitting Potential

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