Pitting corrosion behaviour of stainless steel AISI 304 with different tinting colours

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Tinting colours are a problem often arising at the welding root surface of stainless steel pipes. They appear if a certain residual oxygen content is in the reducing N_2/H_2 purge gas. Different tinting colours are directly connectable to the thickness and the degradation of the chromium oxide layer. For the artificially produced different tinting colours in air, the reduction of the corrosion resistance is evaluated, to determine the critical residual oxygen content. The tinting colours show a change of the corrosion potentials. The investigations are conducted on the most common stainless steel type AISI 304 / 1.4301 of surface conditions 2B (Skin Pass) and 2R (Bright Annealed) with different tinting colours, artificially produced, using a furnace. Electrochemical linear polarization tests are performed on the tinted samples to investigate their corrosion resistance as a function of the Open Circuit Potential (OCP) and the Break Through Potential (BTP). Therefor a standard three electrode set up in a 1l corrosion cell with a 5% NaCl electrolyte is used. Furthermore, the investigations are aimed to standardize the corrosion testing procedure and parameter finding for future corrosion investigations on stainless steels for different applications depending on their surface condition. After the electrochemical tests the severity of the corrosion attack is evaluated metallographically by measuring the depth and the diameter of the pits.

KEYWORDS: Stainless Steel – Corrosion resistance – Tinting – Linear Polarization – Pitting Corrosion

INTRODUCTION

The corrosion resistance of high-alloyed CrNi-steels is based on a spontaneous surface passivation at Cr contents higher than 12% in oxidizing environments. As a result, a very thin, dense and insoluble oxide layer is formed, which prevents the direct contact between electrolyte and steel. The area beside the weld seam can be divided in zones that are characterized by different temperature curves and peak temperatures. During welding the passive layer is replaced by oxide layers of diminished Cr-content, which become visible in different tinting colors. Their formation is determined by the diffusion of the alloying elements towards the surface. Up to 400°C the passive layers gets thicker, but does not change its composition ([1]–[3]).The thicker oxide layers, which are formed above 400°C (appearing in red, blue and grey-brown colors) have a different composition, due to the changing diffusion coefficients, leading to a so-called duplex-structure of the surface layers. This means that a Fe-rich oxide layer on the outer surface is formed and beneath a Cr-rich layer. With increasing temperature, the diffusion coefficient of Cr is increasing but not to the same extent, which would be necessary to deliver enough Cr from the steel matrix. This effect

is enhanced for longer holding times at peak temperature as well as for slow cooling rates in welding. At the same time, Fe can diffuse through the Cr-oxide to the outer surface. The structures of the thermally formed surface layers of different thickness and colors have a distinct influence on the corrosion resistance, especially the pitting potential. The latter is reduced strongly at the transition from the yellow to the red tinting colors, which are formed at around 600°C and is independent of the stainless steel alloy composition. This effect can be traced back to the formed duplex-structure ([3]–[7]) with very low Cr and high Fe concentration on the surface. Thus, it is essential to remove this type of surface layers to obtain the corrosion resistance of stainless steels ([7], [8]).
The investigations in this study, are concentrating on the reduction of the corrosion resistance by oxide layers (tinting colours) before their removal, determined by the reduction of the OCP and the BTP.

MATERIALS AND METHODS

The examined sheet material AISI 304 (1.4301, X5CrNi18-10) had two different surface conditions: 2B of 1.5mm and 2R of 2.0mm thickness. The surface condition of **2B** called "skin passed finish" (mainly for food industry), is cold-rolled and annealed and gets a smoother surface by a further light rolling between highly polished rollers. The result is a semi-bright grey surface and has a roughness value Ra of 0.1 to 0.5 µm. The surface condition **2R** called "bright annealed finish" (e.g. for precision strips), is cold rolled and afterwards the sheet coil is annealed in a reducing, hydrogen containing, atmosphere that prevents oxidisation of the surface. Since the surface was not in contact with pickling acids, it attains a bright finish with a low roughness value Ra of 0.03 to 0.2µm.

The cylindrical samples of 12mm diameter were manufactured by water jet cutting taken out form two DIN A4 format sheets (625cm^2). Artificial oxide layers, which represent the tinting colors during welding, were produced by means of a Nabertherm P330® furnace without shielding gas at two different peak temperatures of 600°C and 1000°C. The samples were kept in the furnace for 10min at peak temperature, thereafter removed from the furnace for air-cooling. For the investigation of corrosion resistance, the following three states per surface condition are investigated: **Blank** with no artificial oxide layer in as received condition and samples with **tinted** oxide layers produced at **600°C** and **1000°C** for both 2B and 2R sheets. Five samples of each surface condition were investigated. Samples before testing are exemplarily shown in Fig. 1, where the tinting colors due to the different peak temperatures are clearly visible: At 600°C brown with blue shimmer and at 1000°C blue-grey with brown shimmer.

All investigated samples were grinded on the backside to ensure an optimized electrical contact for the sample holder and rinsed with water and ethanol before and after electrochemical testing. The stereo documentation was carried out by means of a Discovery V20® with a Zeiss AxioVision® analysis program before and after testing. The temperature and pH-values of the electrolyte were measured before and after testing, as well.

To investigate the influence of the oxide layers on the corrosion resistance, the method of anodic linear polarization was applied. The Open Circuit Potential (OCP), as well as the polarization curves were recorded. From the latter the brake through potential (BTP) as well as the passive range (BTP minus OCP) were further determined.

For the measurement of the potentials and the corrosion currents an Autolab PGSTAT128N® potentiostat with the operation program Nova 1.11® was utilized. For the anodic polarization tests a 1l corrosion cell with a standard three-electrode setup was used, consisting of a working electrode, a counter electrode and a standard electrode. The working electrode exists of each cylindrical sheet sample investigated, fixed in the sample holder, which defines a tested surface area of 1cm^2 by a washer. The counter electrode consists of the material AISI 316L (1.4404) and as standard electrode a 3M Ag/AgCl electrode was used. As electrolyte a standard 5% NaCl solution was used.

The parameters for the electrochemical tests were the same for all samples and were set after preliminary testing. After determining the OCP for 5 min the polarization was started 250mV below the OCP applying a polarization speed of 10mV/min until a threshold value of $0.05 A/cm^2$ was reached. All measured potentials were converted from 3M Ag/AgCl to standard hydrogen electrode potentials (SHE).

To identify the corrosion attack and the geometry of the pits, additionally light optical microscopy (LOM) using a Zeiss Axio Observer Z2m® was performed on cross sections of the samples. Therefor one out of five samples per investigated condition was analyzed, i.e. cutted, embedded with Struers MultiFast® black resin, grinded with SiC and polished with diamond paste down to a surface roughness of 1µm. For that, the depth and the diameter of the appeared pits were measured and the mean value calculated.

RESULTS

Artificial oxide layers were produced, which represent the tinting colors after welding in the heat affected zone (HAZ). The appeared tinting colors are brown with blue shimmer at 600°C and blue-grey with brown shimmer at 1000°C. According to literature the thickness of these layers should be 75 to 100nm for the former and 125 to 175 nm for the latter ([2], [9]), as seen in Fig. 1.

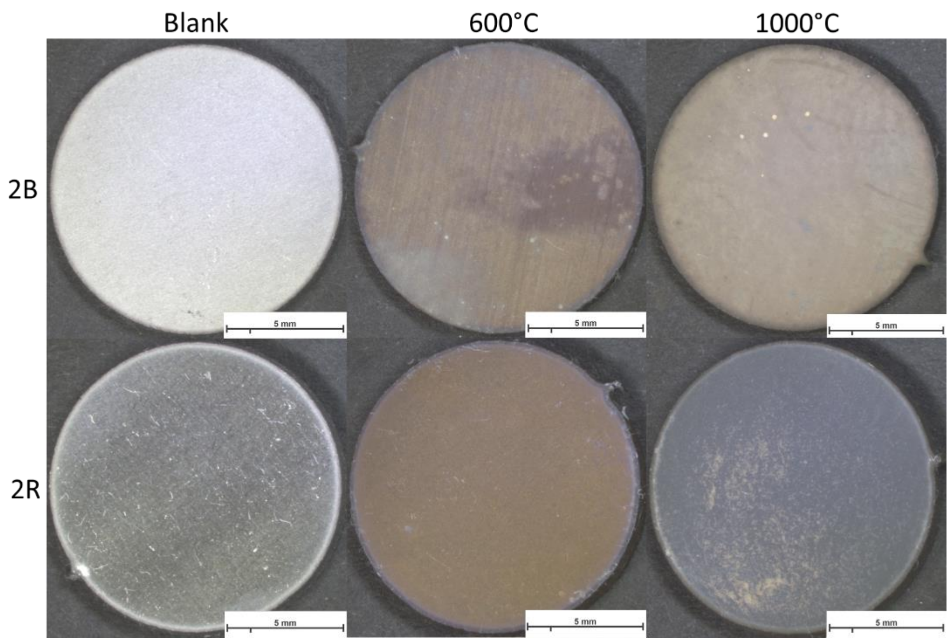

Fig. 1 Samples of 2B and 2R: blank and tinted at 600°C and 1000°C before linear polarization tests.

During the linear polarization tests at 25°C the pH value increased from 6.57±0.35 to 9.60±0.35 for 2B and from 6.31±0.99 to 9.87±0.23 for 2R samples due to the reduction of water and the hydrogen gas bubble formation at the counter electrode. Therefor a similar increase in pH value occurred for both surface conditions. The test duration time varied between 2h 15min to 2h 45 min.

Linear polarization curves showed similar behavior for 2B (skin passed) and 2R (bright annealed), tinted at 600°C and 1000°C. A significant shift of the curves to lower potentials was observed for all tinted samples, compared to the blank ones. This negative shift was higher for 2B samples if compared to 2R, as seen in Fig. 2. The occurring kink in the 2R 1000°C curve, i.e. the intermediate current reduction, is probably due to the observed formation and the following sudden detachment of an adherent and insulating layer of gas bubbles.

The Open Circuit Potential (OCP) is an important parameter that gives a clear image of the behavior of the sample in the corrosion medium. The more positive the value of the OCP, the higher the corrosion resistance. For the performed tests the OCP was positive for the blank samples with 135±2 mV for 2B and 154±52 mV for 2R, therefor 2R shows a slightly higher corrosion resistance in this medium. Comparing the values for tinted samples at 600°C for 2B with -166±24 mV and for 2R with -79±39 mV, similar findings as for the blank samples could be detected, whereas 2R shows a more positive potential and therefor higher corrosion resistance. For tinting at 1000°C the OCP values were found for 2B at -138±28 mV and for 2R at -74±10 mV. All the average OCP values with the standard deviation are shown in **Fig.3**. An overall higher deviation for the values of 2R are found in comparison to 2B, which could be caused by the difference in the surface finish of the received samples. Nevertheless, 2R shows a higher corrosion resistance according to the determination of the OCP values.

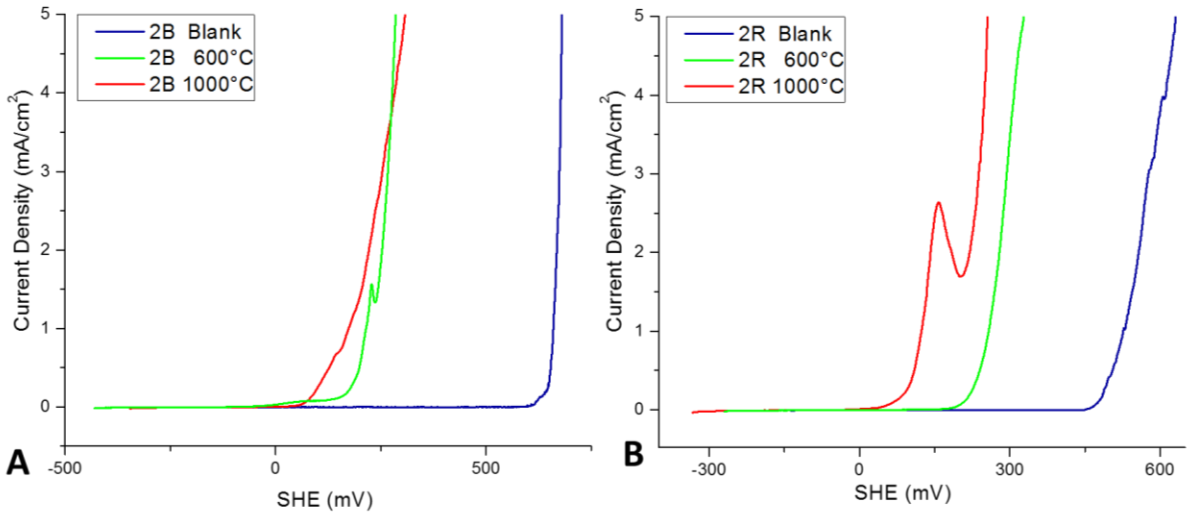

Fig. 2 A) Selected linear polarization curves of 2B in blank and tinted state (600°C and 1000°C); B) Selected linear polarization curves of 2R in blank and tinted state (600°C and 1000°C)

Another indication for the corrosion behavior of the material is the Break Trough Potential (BTP), which is defined as the potential where the rise of current is high compared to change in potential. The mean values and the standard deviation of the tested samples for the BTP are shown in Fig.4. The BTP of **2B** amounts to 623 ±36 mV for blank samples and 171 ±8 mV for tinted samples at 600°C and 95 ±6 mV for tinted samples at 1000°C. The highest BTP was found with blank samples of **2R**, followed by samples tinted at 600°C and the lowest BTP for samples tinted at 1000°C. The BTP of 2R was measured at 650 ± 92 mV for blank samples, 244 ±19 mV for tinted samples at 600°C and 92±17 mV for tinted samples at 1000°C. These findings are consistent with the position and the shift of the polarization curves, in Fig. 2. The deviation of the results was found again higher for 2R than for 2B samples. The former shows higher mean values than the latter at blank and tinted at 600°C conditions. For samples tinted at 1000°C the mean values were almost the same, whereas 2R shows a higher deviation, as noted before.

The difference between the BTP and OCP was determined individually for both 2B and 2R and is equivalent to the so-called passive range, where no significant rise in the current during polarization is measured. The passive range in mean values and standard deviation for both different surface finishes and all three conditions (blank, tinted at 600°C and 1000°C) are presented in Fig. 5. The passive range for 2B was 577 ±50 mV for blank, 199 ±84 mV and 117 ±71 mV for tinted samples at 600°C and 1000°C. The values for 2R amounted to 581 ±112 mV for blank, 252 ±37 mV and 114 ±30 mV for tinted at 600°C and 1000°C. The passive range for the blank samples of 2R and 2B showed a similar mean value, whereas 2R shows a higher deviation. Inverse results showed the samples tinted at 1000°C, whereas similar mean values of the passive region were found too, but 2B showed higher deviation in the results. For the samples tinted at 600°C 2R showed a wider passive range with lower deviation in comparison to 2B.

Generally it is to be noted, that a clear influence of the tinting on the corrosion resistance, determined by the polarization curves, the OCP and the BTP was seen, by the shift of the curves to negative potentials and the lower OCP, BTP and passive regions of the tinted samples.

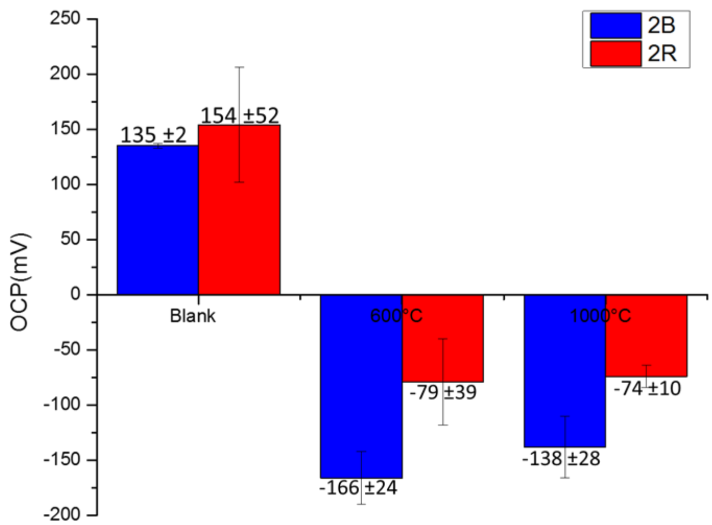

Fig. 3 OCP of 2B (blue) and 2R (red) with blank and tinted at 600°C and 1000°C samples.

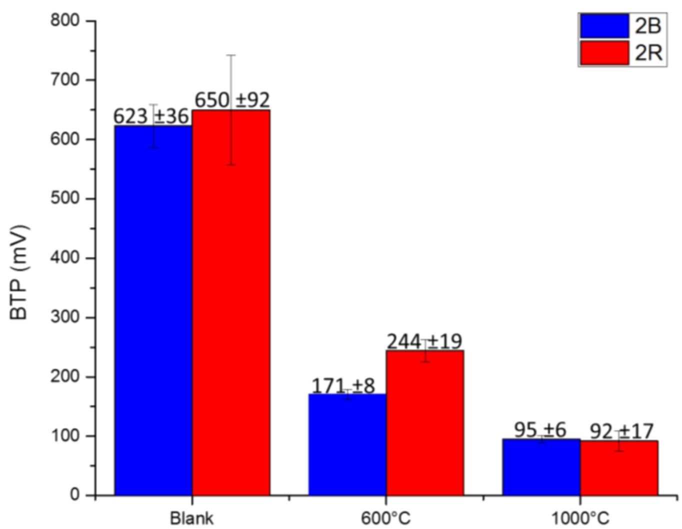

Fig. 4 BTP of 2B (blue) and 2R (red) with blank and tinted at 600°C and 1000°C samples.

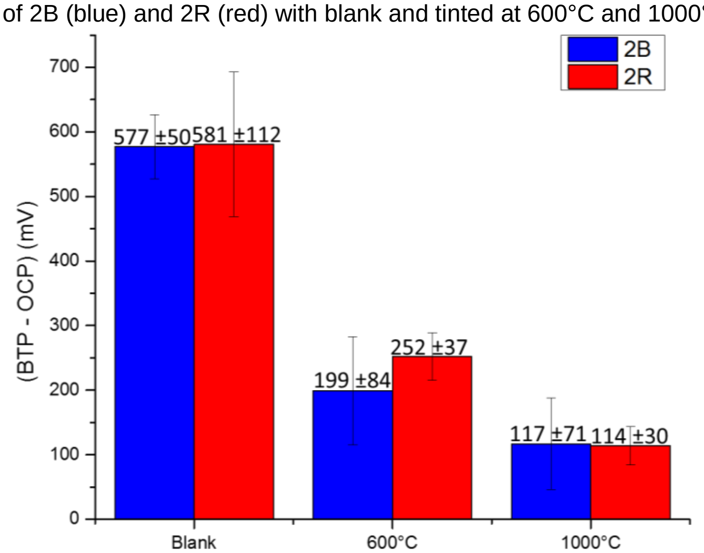

Fig. 5 Passive range (BTP-OCP) of 2B (blue) and 2R (red) with blank and tinted at 600°C and 1000°C samples.

To visualize and to quantify the corrosion attack cross section examinations were conducted in the light optical microscope (LOM). The number of pits, found in the cross sections, was evaluated as well as the mean value and standard deviation of the pitting depth and width for the blank and the tinted samples (600°C and 1000°C), see **Tab.1**.

Tab. 1 Evaluation of number and geometry of pitting cross sections in LOM.

Average and standard deviation for depth and width of the pits for 2B and 2R blank and tinted samples (both 600°C and 1000°C)				
Material type	**Sample type**	**Number of pits**	**Depth (µm)**	**Width (µm)**
2B	Blank	6	76±26	245±83
	Tinted at 600°C	8	29±7	119±49
	Tinted at 1000°C	8	173±233	188±152
2R	Blank	4	76±49	248±133
	Tinted at 600°C	9	61±31	251±162
	Tinted at 1000°C	14	78±111	202±133

In the stereo microscope the surface of the blank samples showed pitting corrosion, see Fig. 6. In detail small pits were found on the surface of the blank 2B samples after testing. In contrast the blank 2R sample (Fig. 6D) showed pits of higher width and the number of pits seems to be the same. These findings are confirmed, as the number of pits found in cross sections of 2B blank was 6 compared to 8 found pits in cross sections for 2R. The quantification of the pits resulted for 2B in a mean depth of 76±26 and a width of 245±83. For samples of 2R a depth of 76±49 and a width of 248±33 were calculated. These results are presented in the diagram in Fig. 6A. The standard deviation was higher for 2R in comparison to 2B samples.

For the samples tinted at 600°C the LOM examinations in Fig. 7 revealed for 2B (Fig. 7B) a similar number of small pits as for 2R (Fig. 7D), while the severity of the attack seems to be higher at 2R samples, appearing by deeper and wider pits. 2B samples showed a similar number of pits as 2R samples, whereas the former were smaller in diameter and lower in depth than the latter. Derived from further LOM examinations 2B samples exhibit 8 and 2R samples 9 pits. The measurements of the geometry gave for 2B samples a depth of 29±7 and a width of 119±49 as well as for 2R samples a depth of 61±31 and a width of 251±162. These results are presented in the diagram in Fig 7A too and confirm the findings from above, which was also proved by Fig. 7C and E.

The corrosion attack seems to be the highest on samples tinted at 1000°C, s. Fig. 8. For 2B samples (Fig. 8B) narrow but deep pits appeared after corrosion testing. The surface is corroded as well, but not as severe, as the 2R samples (Fig. 8D). The LOM investigations showed for the 2B samples 8 and for the 2R samples 14 pits. For 2B samples a mean depth of 173±233 and a width of 188±152 were determined. For 2R samples on the other hand, a depth of 78±111 and a width of 202±133 were found. Overall a very high deviation for all values were determined at 1000°C, as visible in the diagram Fig. 8A.

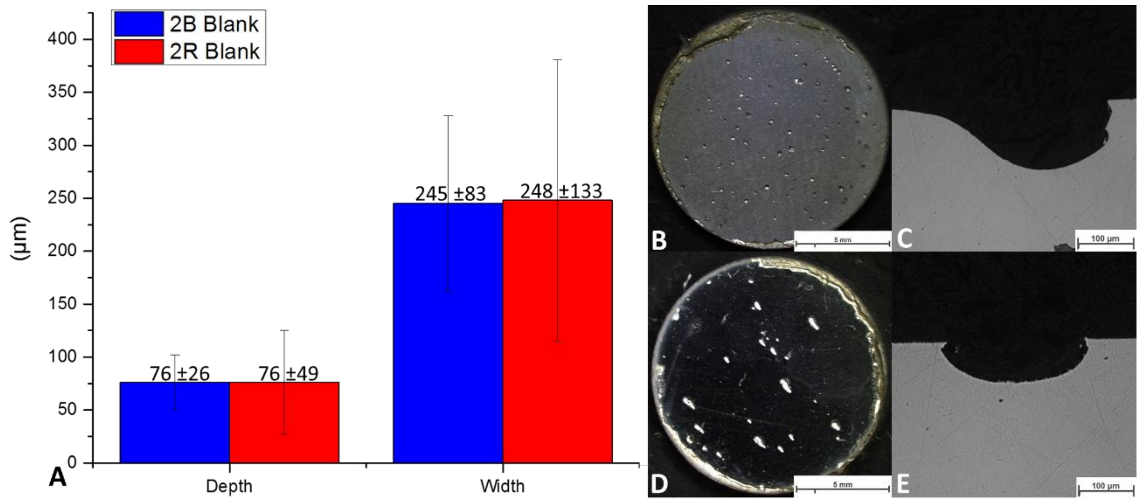

Fig. 6 A) Samples 2B and 2R <u>blank</u>: Mean and standard deviation of pitting depth and width in cross sections; B) 2B after Linear Polarization; C) LOM image of 2B; D) 2R after Linear Polarization; E) LOM image of 2R.

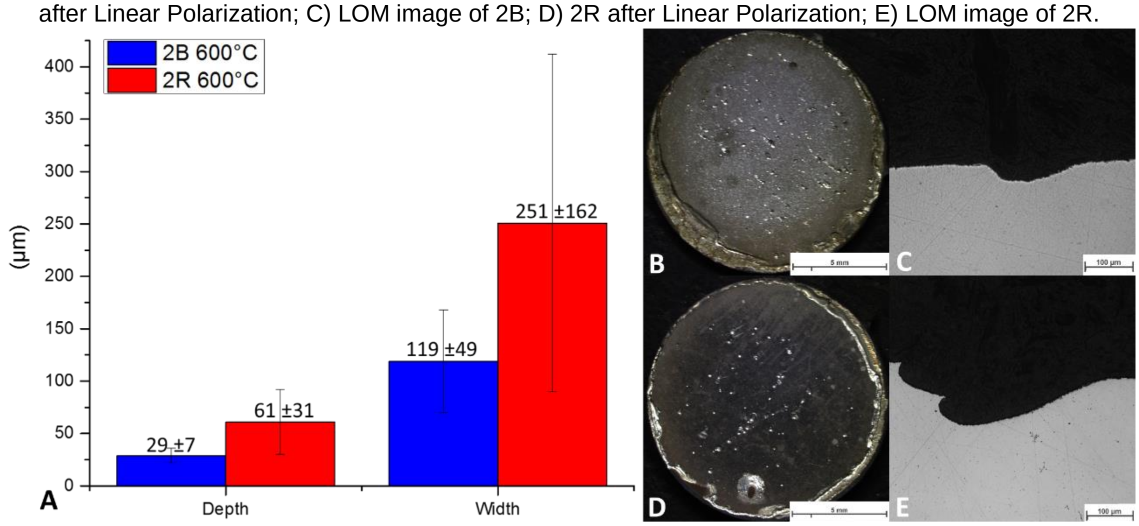

Fig. 7 A) Samples 2B and 2R <u>tinted at 600°C</u>: Mean and standard deviation of pitting depth and width in cross sections; B) 2B after Linear Polarization; C) LOM image of 2B; D) 2R after Linear Polarization; E) LOM image of 2R.

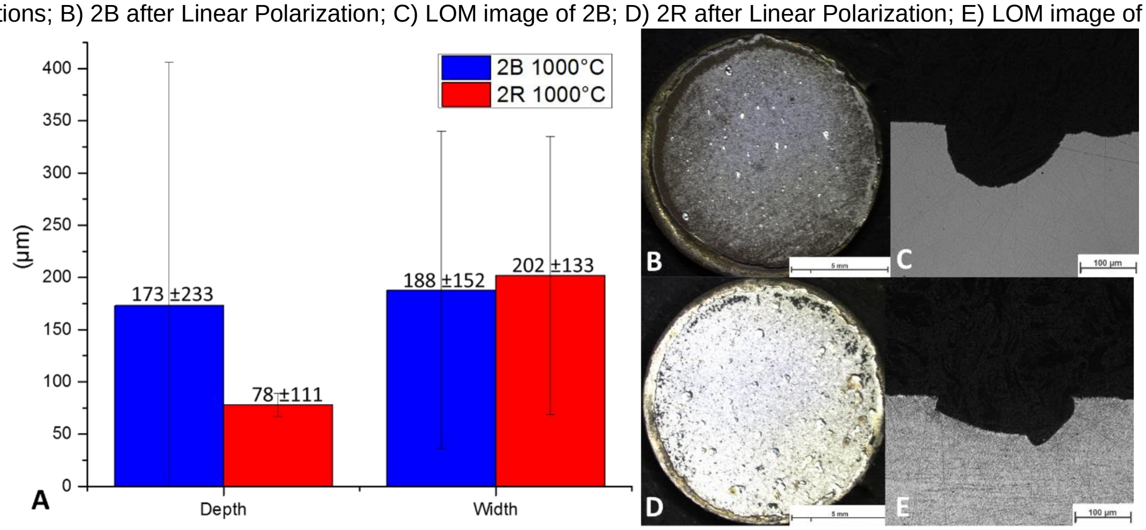

Fig. 8 A) Samples 2B and 2R <u>tinted at 1000°C</u>: Mean and standard deviation of pitting depth and width in cross sections; B) 2B after Linear Polarization; C) LOM image of 2B; D) 2R after Linear Polarization; E) LOM image of 2R.

CONCLUSION

The influence of tinting at two different peak temperatures (600°C and 1000°C) compared to blank (as received) samples of AISI 304 /1.4301 on the corrosion resistance were investigated. Additionally these investigations were performed on two different surface conditions, 2B (Skin Passed) and 2R (Bright Annealed). To determine the corrosion resistance, the samples were linearly polarized and the resulting polarization curves evaluated. To confirm the corrosion attack, also metallography on selected samples was performed.

The 2R samples with bright annealed finish exhibit higher corrosion resistance during polarization tests in 5%NaCl solution than the 2B samples with skin passed finish. This means that the former showed in general a higher Open Circuit Potential (OCP) and Break Trough Potential (BTP) and exhibit a wider passive range (BTP-OCP) than the latter. These results can be traced back to the smooth surface with low roughness of 2R (0.03-0.2 µm) hindering the selective attack of chlorides in forming pits, compared to 2B with a higher roughness of 0.1-0.5 µm. It should be noted that the deviations of these measured values are high for the 2R samples. This is probably due to small surface defects, like scratches, the 2R samples showed.

The artificial produced oxide layers at 600°C and 1000°C in a furnace without shielding gas deteriorate the corrosion resistance strongly. Here again the 2R samples are better in corrosion resistance, compared to 2B. This was verified by higher OCP, BTP and a wider passive range for samples tinted at 600°C. For the 1000°C samples the BTP and the passive range for 2R and 2B are very similar, due to the supposed stronger chromium depletion on the surface.

The evaluation of the corrosion attack, which was identified for all samples as pitting corrosion, showed for all three surface conditions (blank, tinted at 600°C and 1000°C) on 2R samples similar mean values of pitting depth and width, but the number of pits increases with tinting temperature. It must be said however, that the high deviation of depth and width are probably caused by surface defects, i.e. the scratches mentioned above leading to larger pits.

The comparison of the 2B samples in all three surface conditions showed surprisingly for blank a higher depth and width of the pits than for the 600°C tinting. For 1000°C tinting the severest pitting occurred with very high deviation in pit depth and width.

For samples of 2B and 2R tinted at 1000°C the corrosion resistance is strongly reduced as already surface corrosion occurs additionally to the pitting corrosion. This means that there is a strong depletion of chromium not only at the outer surface but also in the adjacent matrix, leading to the described duplex-structure and to a content below the required 12%Cr for a spontaneous surface passivation, what should be investigated further.

It can be concluded that the 2R bright annealed finish shows better corrosion resistance compared to the 2B skin passed finish in linear polarization testing and a constant pitting depth in all three surface conditions. Attention must be payed to exclude surface defects, especially for 2R. Despite the low pitting penetration rate (low pits depth) at 600°C - especially for 2B - it is recommended to remove the tinting color by brushing, pickling and rinsing, to save the corrosion resistance of the AISI 304 stainless steel [10].

ACKNOWLEDGEMENT

We want to express our gratiute to Aperam Research in Isbergues (France) for providing the stainless steel sheet materials.

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