

Determination of critical temperature for pitting corrosion occurrence at welded 2205 duplex-duplex steel

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Abstract: The aim of this paper was determination of the critical temperature at which pitting corrosion occurs in welded 2205 duplex-duplex steel. Its chemical composition and properties are given. Pitting corrosion and the conditions of its occurrence as well as the measures for protection against it have been specially treated. Also, duplex steel welding preparation procedures are described. The welding process of the specimen as well as its properties after welding is given as well. The microstructure of the specimen and its austenite-ferrite ratios were obtained and analyzed. Susceptibility to pitting corrosion was tested in simulated seawater atmosphere. Pitting corrosion resistance tests through conducted surface roughness analysis were performed and discussed for each set of parameters, which included time and temperature. The results showed that temperature elevation has a significant influence on pitting corrosion occurrence. Measured critical temperature value for pitting corrosion occurrence at welded 2205 duplex-duplex steel in simulated seawater conditions was 40 °C.

1. Introduction

Considering the fact that both, austenite and ferrite phase influence the duplex steel properties, it is useful to determine their ratio. The heat introduced during welding process can deteriorate the duplex steel structure, so it is of a great importance to control the temperature during welding. The difficulty with duplex steels welding is the heat affected zone, where lower corrosion resistance, decreased toughness or post-welding cracks may occur. To avoid this, defining of proper welding technology is needed by reducing time duration in critical temperature interval. It is necessary to control the heat input for every layer [1]. During welding processes at elevated temperatures, the whole microstructure in heat affected zone becomes ferritic. If certain ferrite-austenite transformation should not occur, negative influences on material properties emerge, toughness and corrosion resistance reduce. Therefore, different nickel-based added materials (3-4 % nickel) are used, which favour austenite forming in weld with keeping the austenite/ferrite ratio in balance. In heat affected zone, this control is not possible; moreover, achieving the relevant phase balance depends on certain skills and welding conditions [2, 3]. By increasing the temperature during welding, ferritic area expands. There, just beside the melting line in heat affected zone, rough ferrite grains

form surrounded by austenite matrix. By inducing a small amount of heat in welding process, quick cooling occurs which results in forming of mostly ferrite phases in heat affected zone. Slow cooling may lead to carbide, nitride or iron-nickel intermetallic compounds extraction, and brittleness at 475 °C [3]. Therefore, optimal temperature at which these two phases will be in balance should be found.

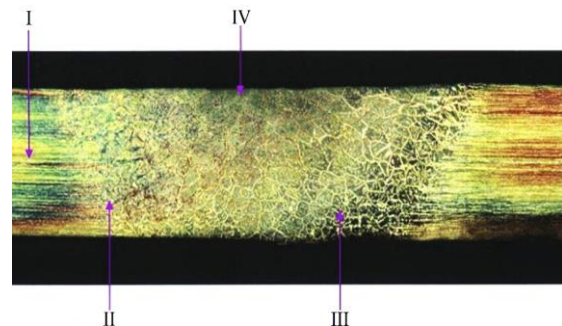


Figure 1. Macrostructure of welded 2205 duplex-duplex steel consists of: I. – base metal macrostructure; II. – low - temperature heat affected zone macrostructure; III. – high - temperature heat affected zone macrostructure; IV. – weld macrostructure [4]

Due to the low carbon content, occurrence of inter-crystal corrosion is reduced. Duplex steels in general have very good resistance to pitting corrosion due to low carbon content and high content of chromium, molybdenum and nickel. If the microstructure of duplex steel contains increased level of ferrite phase, or nitride precipitations occur in large ferrite grains, this will have a negative influence on materials pitting corrosion resistance. Welding behaviour of duplex 2205 stainless steel was analyzed, where comprehensive study was done right on the effect of welding on corrosion, mechanical properties and subsequently on the microstructure of 2205 stainless steel, pointing out the necessary parameter balance for the purpose of providing certain corrosion resistance, moreover showing primary pitting corrosion occurrence at HAZ [5]. Corrosion behaviour of duplex steel welds after short-time heat treatment was also analysed. In the tested range from 1020 to 1150 °C with holding time of 3 minutes, the highest pitting corrosion of the welds was obtained while heat treating at 1080 °C [6]. It was also established that the ferrite phase in the HAZ was the weaker phase, which confirms the thesis how much the HAZ in the 2205 duplex steels is sensitive structure wise and how it affects its corrosion resistance. Furthermore, ambient temperature pitting corrosion on 2205 duplex steels was analysed with the use of bipolar electrochemistry method, where corrosion pits formed by selected dissolution of ferrite phase [7]. The observations also showed that pit nucleation typically occurred at the ferrite–austenite interface, with pit growth via dissolution of the ferrite phase. The pitting corrosion occurrence of duplex 2205 steel welded by filler metal 2209 was also tested, after exposure to service temperatures [8]. The results showed that severe pitting corrosion and the largest metal loss occurred while heat treating at 850 °C, with holding times of 1 and 3 h. This reason for this is the presence of large amounts of intermetallic phases within the matrix at this temperature, which point out the importance of the particular intermetallic compound occurrence in 2205 duplex steel weld joint and their influence on 2205 duplex steel corrosion resistance or susceptibility. Corrosion behaviour of laser beam welded 2205 duplex steel in simulated body fluid was analysed as well. The results indicated that laser-welded AISI 2205 duplex stainless steel showed enough corrosion resistance in case of using it as a short-term implant in human body, which emphasise the usage possibilities of welded 2205 duplex steels in potential corrosive (organic) environment [9]. Duplex steels are commonly used in shipbuilding industry, so base metal and welded joints can be in direct contact with seawater. Nevertheless, poorly machined surfaces are generally not recommended for the marine exposure due to their grooved surface profiles which will endanger the

material's life drastically. Shot peening, laser shock peening and friction stir processing are significantly enhancing the surface properties of duplex 2205 steels which are strongly recommended in the corrosive environment [10].

The possibility of corrosion occurrence in these steels would significantly influence the stability and endurance of vessels, moreover maritime constructions in general. In experimental work, the susceptibility of welded duplex-duplex steel to pitting corrosion was tested, in simulated seawater conditions.

2. Experimental work

The experimental work was conducted in chemical laboratory at Brodosplit d.d. Shipyard Company. The specimen was previously welded at manufacturing plant at Brodosplit, with delta-ferrite content determination. The macrostructure of duplex steel welded joint consists of characteristic areas, showed in Figure 1. Specimen was then prepared and submerged into simulated seawater atmosphere solution.

After being kept in a solution for a certain time, measurements and determination of pitting corrosion existence were done.

2.1. Welding of steel plate

As the base material for specimen making, duplex stainless-steel 2205 (UNS S31803) was used, which chemical composition is given, Table 1.

Table 1. Chemical composition of 2205 duplex steel by mass proportion [11]

wt	C	Mn	Si	P	S	Cr	Mo	Ni	N
						min:	min:	min:	min:
						21.0	2.5	4.5	0.08
2205 (S31803)	max:	max:	max:	max:	max:				
	0.03	2.0	1.0	0.03	0.02				
						max:	max:	max:	max:
						23.0	3.5	6.5	0.20

Sheet thickness from which specimen was made was 12 mm. Welding was done by MAG process with powder-filled cored wire according to EN ISO 4063:2012. Wire diameter was 1.2 mm, and gas flow rate 18 l/min. The weld form was "V", in horizontal position. Inert gas mixture argon with 18 % carbon dioxide was used. For quality root welding purposes ceramic backing was used. This way, weld root could be welded with higher current which insured better weld quality. Steel plate was welded in eight layers, Figure 2.

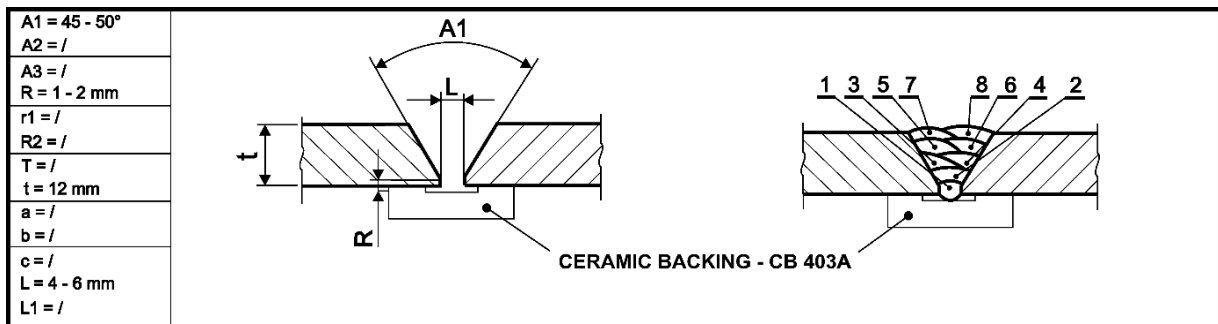


Figure 2. Welding preparation parameters with welded layers' scheme

2.2. Surface preparation of welded specimen

After the welding was completed, the specimen was cut out of the welded plate with the use of Struers LABOTOM-5 manual cut-off machine with coolant. Since no additional heat has been introduced, no apparent changes in microstructure have occurred. Specimen surface was then treated for rough edges, grease, dust and other impurities. Surface was then treated mechanically, to obtain smooth finish in order to remove any possible pits caused by pitting corrosion. For mechanical treatment, grinding and polishing device with rotating discs was used. To avoid specimen overheating, water was used. Grinding was done with grit designation P60. Then, finer grinding papers were used to a final P1500 grit designation, Figure 3.



Figure 3. Polished specimen prepared for further testing After all rough edges were eliminated, further testing and analysis of polished specimen were conducted.

2.3. Determination of delta-ferrite phase in welded specimen

If welding procedure was not done properly and the material is left with too much ferrite content, toughness decreases as well as corrosion resistance. This way stainless steel loses its primal properties. Therefore, it is necessary to determine the ferrite content after the welding is done. Ferrite content at welded duplex steel materials should be between 30 % and 65 %. The range

can be somewhat wider or narrower but never outside the interval 20-70 %. To make communication easier worldwide, internationally used term Ferrite Number [12] (FN, e.g. FN 30), is accepted for the purpose of marking the delta-ferrite content in stainless steel welded joints. Ferrite Number is commonly used as an indicator for certain welding characteristics, among which is weld resistance to hot cracking. Ferrite Number is not equal to volumetric content of ferrite (%). Although real content of ferrite cannot be measured precisely, relevant estimate of ferrite content can be obtained by dividing the Ferrite Number with factor f (% ferrite = FN/ f), which is dependable on iron content in weld metal, Figure 4.

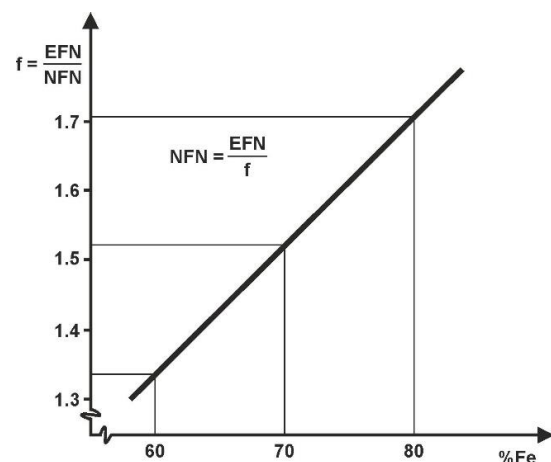


Figure 4. Factor f dependence on Fe percentage in weld metal [13]

Measuring surface must be thoroughly prepared and flat enough to ensure proper connection of the test probe. In this regard, weld area must be smooth, which was done by brushing. During the brushing process, no micro structural changes (martensite forming, colouring) should take place. Measuring area distance should be 40 mm with minimal width of 5 mm. There should not be

any leftovers from welding arcs, as well as impurities, magnetic particles, dust or lubricants.

Determination of delta-ferrite was done by FERITSCOPE FMP30 instrument. Prior to measuring, the instrument was calibrated by secondary standard in relation to EN ISO 8249. As ferrite is not evenly distributed in the material, the obtained results from one welded joint can vary from one measuring point to another. Therefore, measuring was done at 6 evenly distanced points distributed on the central line of measuring area.

Ferrite Number is an arithmetical mean of 6 individual measures, rounded to the next whole number. Measuring was done at room temperature of 21 °C. Measuring surface should not be exposed to any shocks or vibrations during measuring process. Welded specimen was submitted to ferrite content determination, and it fulfilled the condition of minimum, therefore maximum content. The results were presented for base metal, heat affected zone and weld. The microstructure was developed by etching in solution prepared by adding 5g of iron (III) chloride in the mixture of 10 ml of hydrochloric acid and 100 ml of water. After welding, mechanical treatment and ferrite phase measuring of the specimen, it was submitted to surface etching by the solution that simulates seawater atmosphere. Magnetic mixer that was used is IKA C-MAG HS 7. Pitting corrosion occurrence detection was conducted by MarSurf PS1 instrument made by Mahr GmbH Company.

3. Results and discussion

In base metal of prepared specimen, two-phase microstructure of duplex steel is clearly visible, with equal phase ratios, Figure 5. Average measured value of ferrite on the left side of the weld was 53.8 %, and 53.1 % on the right side. Values are satisfactory considering the optimal ferrite phase interval of 30-65 %. Unlike the microstructure in base metal, phases in heat affected zone are not clearly and evenly distributed. Temperature influence on material microstructure is visible, Figure 6. Larger grouping of phases occurred with consequently larger grains. The microstructure is not homogenous as it is in the base metal, which leads to the conclusion that mechanical properties in this zone are reduced as well as the corrosion resistance. The line that divides heat affected zone from the base metal is visible. Since duplex steels (austenite phase especially), are poor heat conductors, this line is particularly expressed. Measured ferrite values in the heat affected zone are 46.7 % on the left side and 45.8 % on the right side of the weld. The values are, as in base metal, in optimal range.

In weld microstructure, a clear difference in relation to base metal is visible, Figure 7.

The grain growth is obvious, and the measured ferrite content is somewhat lower. The ferrite average value is 40.9 % which is still satisfactory. Moreover, in weld zone, as well as in heat affected zone, grain growth

consequently brings reduced mechanical properties and corrosion resistance.

The measurements of ferrite phase are done in all three zones of the material.

The optimal ferrite value is established in every zone. In base metal, as well as in heat affected zone, measurements were done on both sides of the weld to be sure that the ferrite content is satisfactory through the whole specimen area. In both zones, the ferrite content was almost the same on every side.

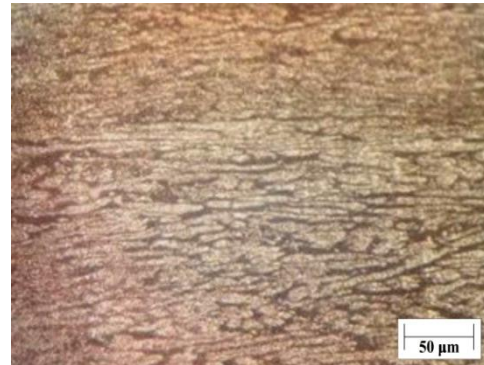


Figure 5. Base metal microstructure

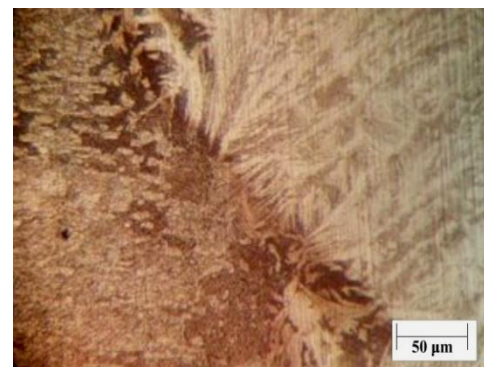


Figure 6. Heat affected zone microstructure

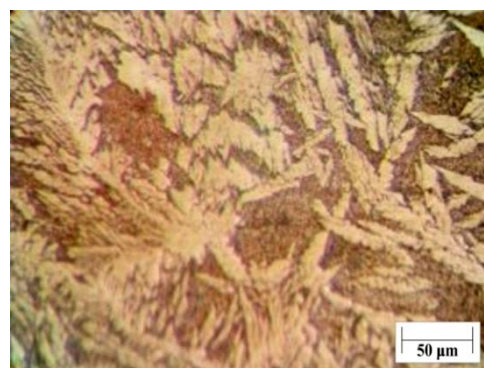


Figure 7. Weld microstructure

Specimen was submitted to surface etching by the solution that simulates seawater atmosphere. Iron (III) chloride was used [14]. The solution contained 5 g of dissolved iron (III) chloride in 10 ml of hydrochloric acid and 100 ml of water, as it did for microstructure development shown earlier in the paper. The specimen was put into chemical container with prepared solution. The aim was to submit the specimen to simulated seawater conditions at three different temperatures. Test was conducted at 25 °C, 30 °C and 40 °C for the period of 72 hours, Figure 8.

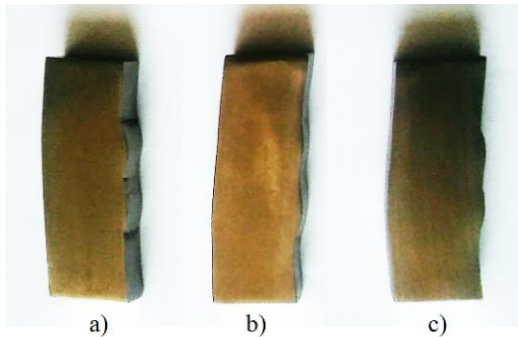


Figure 8. Specimen images after surface treatment for 72 hours with iron (III) chloride at temperatures a) 25 °C, b) 30 °C, c) 40 °C

Due to the relevance of the obtained results, after each testing regime was conducted, specimen was grinded to a final P1500 grit designation, polished then rinsed with 96 % ethanol and dried to its initial state. Moreover, roughness measurements were repeated as well, to ensure that specimen is brought to its original state and ready for the next testing cycle.

MarSurf PS1 instrument enabled simple surface roughness measurement. Path distance includes starting length "run up" which enables feeler carrier on measuring instrument to accelerate to certain constant velocity, and final length "run out" at which the feeler stops. Only the part of the L_t distance is measured

therefore used for roughness grading and determination. L_n , in general, is mostly consisted of several referent distances L_r [15], Figure 9.

As it was pointed before, pitting corrosion is expected to occur in heat affected zone first, therefore in large-grained structure. Determination of critical temperature for pitting corrosion occurrence was initiated with specimen treated at 25 °C. MarSurf PS1 instrument has a measuring console which is its standard equipment as well as the integrated calibration block. Measuring feeler (2 μm in diameter) is made from diamond. It pressures the measuring area with the force of 0.7 mN.

Surface roughness has been the subject of experimental and theoretical investigations for many decades [16, 17]. Surface roughness measurements are expressed by parameters R_a , R_z , R_x or T_p . Parameters are obtained by measuring profiles from deepest valley to their highest peak with the combination of peak frequency mark in certain area. All roughness parameters that were used are defined by the ISO 4287 standard.

Referent distance or plain is a chosen dimension on which surface roughness is established, where no other imperfections are considered; such as chamfers, cavities, form deviations and others. Referent distances values are standardized [15] and they are: 0.08, 0.25, 0.80, 2.5, 8.00 and 25.00. Referent distance used in this work was 0.80 mm, due to the specimen characteristics.

Selection of instrument parameters was done in relation to the tested specimen. The finer surface finish was; the lower instrument border values were chosen. Furthermore, measuring distances depend on testing specimen distance itself. For this particular testing, chosen border values were 0.8 mm, with measuring distance 2.4 mm. The instrument was positioned on the specimen; roughness was measured by feeler movement on referent distance L_t which was 2.4 mm. After the feeler had passed the referent distance, roughness measurements were ready for analysis. As it was mentioned earlier in the paper, the occurrence of pitting corrosion is expected in heat affected zone, so that area was particularly surveyed.

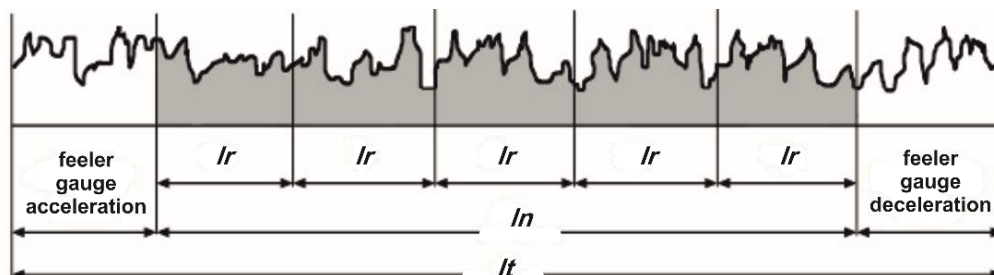


Figure 9. Characteristic distances of 2D roughness profile [15]

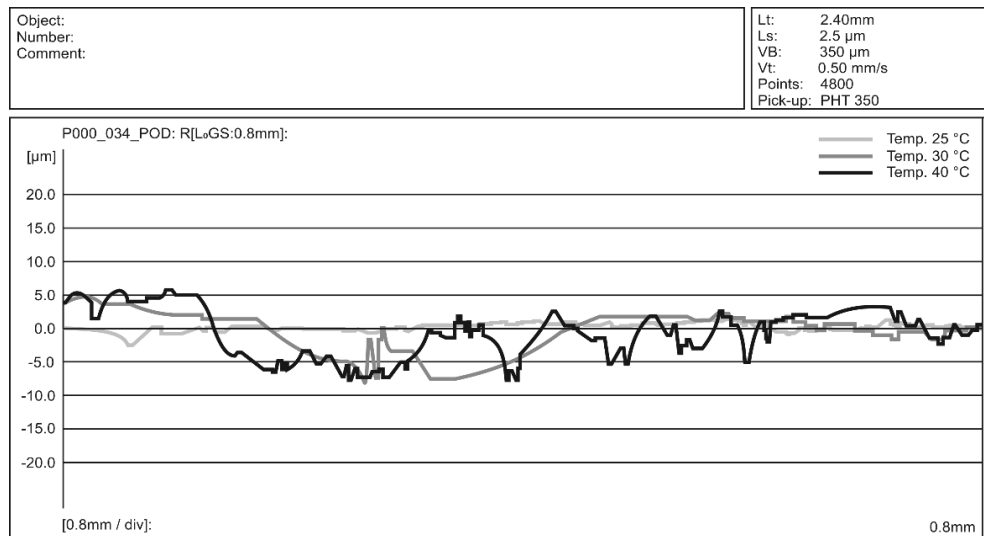


Figure 10. Surface roughness of the specimen treated in iron (III) chloride solution for 72 hours at 25, 30 and 40 °C

With no surface anomalies detected by visual inspection, neither the testing provided any anomalies in terms of pitting corrosion. The surface roughness measurement diagram for the specimen treated in iron (III) chloride solution for 72 hours at 25, 30 and 40 °C was obtained, Figure 10.

On Figure 10, it can be perceived that the biggest surface roughness deviation is noted at $T = 40$ °C. The deviations at this temperature are present regardless of specimen measuring position; base metal, weld zone or heat affected zone, with somewhat different, but nevertheless critical values.

MarSurf PS1 instrument read an arithmetic mean deviation of the assessed profile Ra , and maximum depth of the profile irregularity Rx , according to the instrument nomenclature. Ra value was 0.438 µm, while Rx was 5.3 µm. These results do not point out any pitting corrosion occurrence, according to ASTM G48. It can be stated that welded duplex 2205 steel treated in iron (III) solution for the period of 72 hours at 25 °C is pitting corrosion resistant. After bringing the specimen to initial state, testing was continued with same parameters apart from the temperature, which was elevated to 30 °C. Surface roughness results for the specimen submerged in iron (III) chloride solution for the period of 72 hours at 30 °C did not show any substantial occurrence of pitting corrosion. However, significant increase of Rx value was noted, which was 19.4 µm, and more than 3.5 times greater than in the first cycle. As it was expected, biggest peak values appeared in heat affected zone in which grain growth took place due to the welding process heat input. Values are not critical, but they do point out that temperature has a significant impact to surface roughness increase, therefore pitting corrosion occurrence.

The values measured at 40 °C pointed that pitting corrosion developed significantly. Rx value was 28.6 µm, which is, according to ASTM G48 standard, considered as pitting corrosion presence. This standard suggests that border value of Rx for pitting corrosion occurrence is 25 µm. Therefore, all values beyond 25 µm are considered as pitting corrosion existence. Surface anomalies are clearly noticeable from the diagram. Even before the specimen was taken out of the solution, by visual inspection it was clear that the surface did not stay smooth; moreover, the elevated temperature effect was noted, Figure 11. Pitting corrosion development is noticeable at the weld edges in heat affected zone, as it was expected.



Figure 11. Specimen image after iron (III) chloride solution treatment for 72 hours at 40 °C

4. Conclusion

In this paper, critical temperature for pitting corrosion occurrence at 2205 welded duplex-duplex steel was determined. According to the ASTM G48 standard,

border value of R_x for this type of corrosion occurrence is 25 μm . All values below the proposed one are not considered as pitting corrosion occurrence, which does not mean that they should be neglected. This type of corrosion is very hazardous because it is hardly visible. Once it evolves, then it is mostly too late for reparations. Therefore, it is important to survey every change in surface roughness since it is a parameter for potential pitting corrosion development. The testing was done in simulated seawater atmosphere. Considering the fact that average sea temperature is below 40 °C, it can be concluded that welded duplex steels are resistant to pitting corrosion in real conditions. From the diagrams obtained by Marsurf PS1 instrument, it is visible that temperature has a significant influence on pitting corrosion occurrence. At treatment with iron (III) chloride at 25 °C, surface roughness was almost negligible. With temperature increase by only 5 °C, significant increase in surface roughness is perceived; therefore, potential spots for pitting corrosion occurrence are noted. By elevating the temperature to 40 °C, definite occurrence of pitting corrosion phenomenon is recognized. From conducted experiments, it can be concluded that temperature has a significant influence on pitting corrosion occurrence and that the critical temperature value for pitting corrosion occurrence at welded 2205 duplex-duplex steel in simulated seawater conditions is 40 °C.

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