INFLUENCE OF SURFACE TREATMENT ON CORROSION RESISTANCE OF Cr-Ni STEEL

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Abstract:

This paper presents test results of the resistance towards pitting corrosion of AISI 304L stainless steel, after heat input by TIG welding process and subsequent chemical and electrochemical surface treatment, upon which the efficiency of "classical" and "environmentally friendlier" heat tint removal solutions was studied.

1 Introduction

Corrosion resistance of stainless Cr-Ni steels is based on the spontaneous development of the passive Cr_2O_3 film of 1-10 nm in thickness, which occurs almost immediately on the surface of these steels in media with sufficient content of oxygen, at the minimum of 10.5 wt% Cr. Different surface inhomogeneities and damage to the oxide layer may impair the passivity of stainless steel and transform the surface of steel in the electrochemically active state liable to different, usually local, corrosion phenomena [1, 2]. Structures from these types of steels are usually made by welding. Beside the structural changes occurring in the weld metal and heat affected zones as a result of heat input during welding, due to the chemical oxidation of the surface (at temperatures above roughly 300 ºC), thermal oxides are formed with different chemical composition and thickness from the original passive oxide film. This phenomenon results in interference colours and finally in generation of an opaque film with greater thickness than the original oxide film, table 1 [3].

Table 1. Heat tint colors in correlation with the thickness of thermal oxides [3]

Heat tint colors	achromatic	chromium yellow	straw yellow	gold yellow	brown red	cobalt blue	light blue	achromatic	brown grey
Temperature, °C	room	< 400	≤ 400	500	650	900	1000	1100	1200
Film thickness, nm	≤ 5	≤ 5	25 – 50	50 – 75	75 – 100	100 – 125	125 – 175	175 – 275	> 275

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A newly formed thicker oxide layer is inhomogeneous, contaminated with various particles and compounds, and beneath it, there lies a chromium depleted zone which further impairs corrosion resistance in that weld area, which is already metallurgically different from the base metal outside the weld. Since the volume of such oxide layer is larger than the volume of metal, and because of the formation of nuclei of oxide matrix (Fe, Cr, Ni)$_x$O$_y$ (if oxygen (O_2) is available or its compounds (H_2O, CO_2)) with the ratio of y/x = 1-2, compression stresses cause breaking of oxide film, i.e. initiation of defects in the passive film occurs. Heat tints represent areas of significantly degraded corrosion resistance, and very often, corrosion phenomena are initiated in the heat tint zones, usually in the form of pitting corrosion [4, 5]. According to the three-layer passive film model of the austenitic stainless steel formed in the acid media (Figure 1), which was introduced in the seventies of the 20th century, the outer part of the film seems to be a hydroxide layer which is located above the oxide layer [6]. An oxide–hydroxide layer is formed above the interfacial nickel rich layer, which was developed as a result of selective oxidation of iron and chromium.

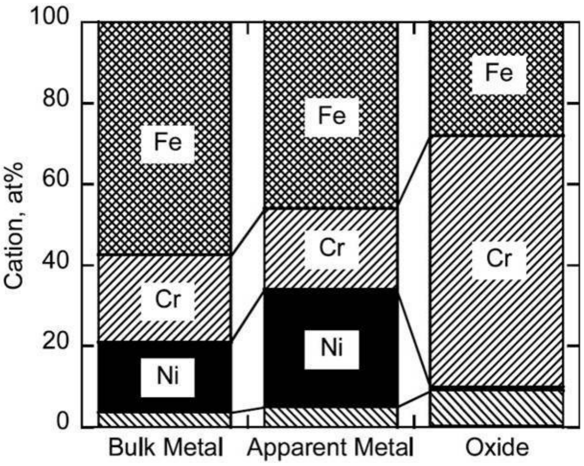


Figure 1. Schematic representation of passive film on stainless steels [6].

Cracks and defects in the oxide layer expose stainless steel surface to aggressive electrolyte (such as $FeCl_3$). Hydrolysis (i.e. $MeCl_3 + 3H_2O \leftrightarrow Me(OH)_3 + 3HCl$) reduces pH values due to production of strong acid, and with the propagation of pits, products (like hydrated chlorides) with up to 20 times larger volume than that of original metal are formed. This altogether provides conditions for the autocatalytic process of deterioration [5]. To restore the corrosion resistance of stainless steels after welding, it is necessary to remove heat tints and the chromium depleted zone which lies beneath them.

This is usually carried out by mechanical, chemical and electrochemical processes, which are often combined. The removal of heat tints using mechanical procedures is usually carried out with the use of appropriate grinding tools so as to completely remove thermal oxides and the oxide layer, after which the steel surface (an oxide film) in contact with oxygen heals itself again. After such treatment, it is advisable to carry out the process of chemical passivation. The removal of heat tints using chemical processes may be carried out locally in the weld areas using etching pastes, by spraying, or by immersing the entire structure in a pickling bath. The electrochemical process of heat removal is carried out by applying alternating current, while the use of direct current has the polishing effect. In chemical and electrochemical heat tints removal methods, "environmentally friendlier" solutions are experiencing an increasing use. Unlike "classical", "environmentally friendlier" solutions contain some of the most harmful compounds like HF, HNO_3 or H_2SO_4 in a much lesser extent, or not at all, which makes them less harmful to the environment and human health. During the etching of the surface with "environmentally friendlier" solutions, evaporation of harmful NO_x and HF fumes is considerably less, which is ecologically very advantageous [1, 2, 4].

2 Experimental

In the experimental part of the paper, the focus is on the influence of chemical and electrochemical surface treatment of austenitic stainless steel AISI 304L (EN 1.4306) towards pitting corrosion resistance after heat input, and on the efficiency of "classical" and "environmentally friendlier" heat tint removal solutions.

Table 2. Typical chemical composition of AISI 304L (EN 1.4306) [7]

C	Si	Mn	P	S	Cr	Ni
0.03	1.00	2.00	0.045	0.030	18.00-20.00	8.00-12.00

2.1 Development of heat tints

On the samples measuring Φ16×1 mm, thermal colorations were achieved with spot TIG heat input without using filler metal (Figure 2).

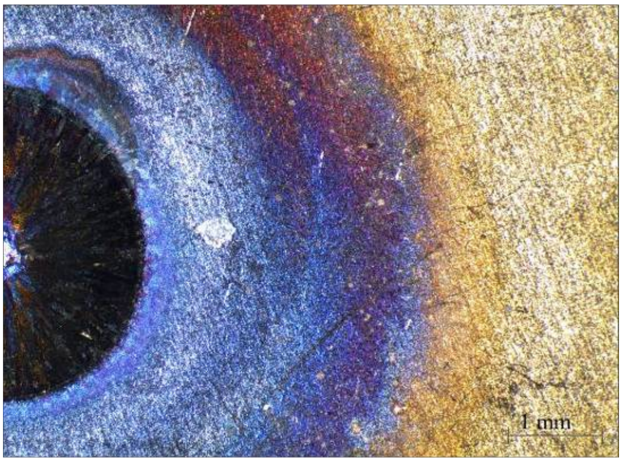


Figure 2. Heat tints after dotted TIG heat input on samples prepared for testing according to ASTM 61.

While on the samples measuring 150×100×3 mm, surfacing of two build up TIG welds measuring (l×w): 50±2 mm × 6±2 mm was carried out using EZ-TIG 308LSi Φ1.6 mm filler metal, Figure 3. TIG parameters were: I = 85 A, U = 9-11 V, shielding gas 100% argon, gas flow rate 7-8 l/min, arc height 3-4 mm.

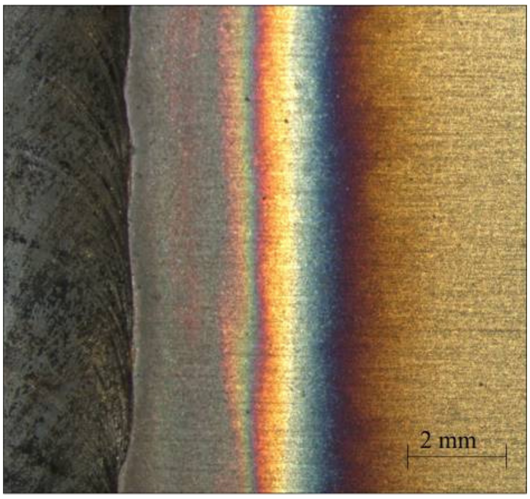


Figure 3. Heat tints on samples prepared for pitting corrosion testing according to ASTM G48.

2.2 Preparation of samples

The removal of heat tints was performed by chemical and electrochemical heat tint cleaning methods using "classical" and "environmentally friendlier" solutions for subsequent surface treatment. "Classical" solutions are very efficient in the removal of heat tints, but they also contain high levels of chemical compounds like HF, HNO_3 or H_2SO_4, which are very harmful to the environment and human health. Efficiency of these solutions was compared with the efficiency of the newer "environmentally friendlier" solutions which contain substantially fewer or none of the mentioned hazardous chemicals.

In order to draw comparisons, sample preparation for testing according to ASTM G48 was conducted in such a way that only one build-up weld (only one half of the surface) was treated, while the other weld remained untreated (with heat tints). The surfaces of the samples, which were prepared for the electrochemical corrosion testing in accordance with ASTM 61, were fully cleaned. For each of the procedures, one "environmentally friendlier" and one "classical" solution was used. In chemical surface treatment, heat tints were removed by the use of "classical" solution, in cca. 40 minutes, while by the "environmentally friendlier" solution it took cca. 80 minutes (for the same task) to be carried out. The temperature of solutions used in these tests was 20 ± 2 ºC, and the results of cleaning efficiency are shown in Figure 4.

2.3 Testing of corrosion resistance

Corrosion resistance testing was conducted in the Laboratory for materials protection at the Faculty of Mechanical Engineering and Naval Architecture in Zagreb, using tank immersion according to ASTM G48 in the 10% solution of $FeCl_3 \times 6H_20$, during 24 hours, and using an electrochemical method of cyclic polarization in 3.5% solution of NaCl according to ASTM 61, upon which potentiostat EG & G Model 323 and software package EG & G Corrosion Software 352 were used for collecting data. During both tests the temperature of test media was 20 ± 2 ºC.

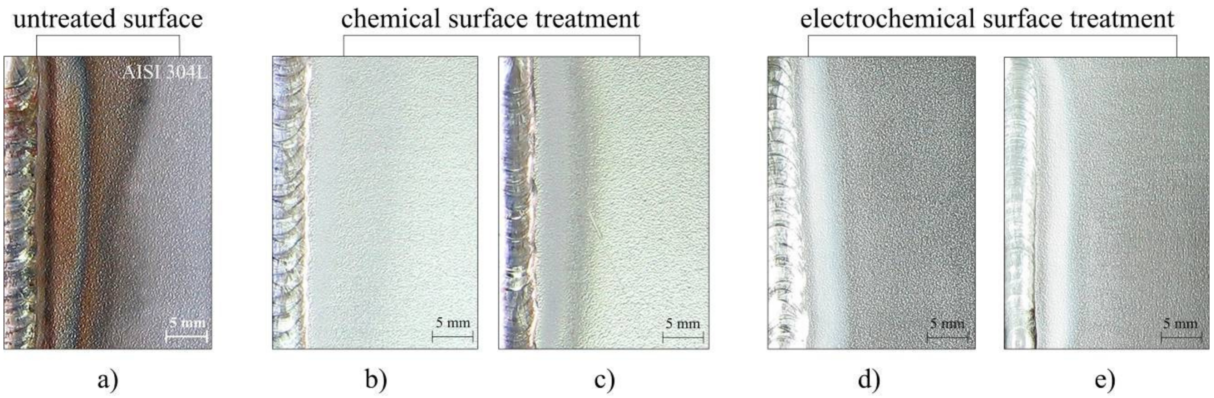


Figure 4. Presentation of cleaning efficiency: a) before surface treatment, b) "classical" solution 1, c) "environmentally friendlier" solution 1, d) "classical" solution 2, e) "environmentally friendlier" solution 2.

3 Test results

3.1 Testing in accordance with ASTM G48

Test results of the resistance towards pitting corrosion indicate that corrosion resistance depends significantly on the state of the surface. An insufficiently cleaned surface, on which thermal oxides were still present, had the lowest resistance towards pitting corrosion, and pitting damage occurred predominantly in the areas of thermal oxides farthest from the middle of weld beds, in the area of color interference of 1st. order. Test results also indicate that the effectiveness of applied solutions has a significant impact on the pitting resistance.

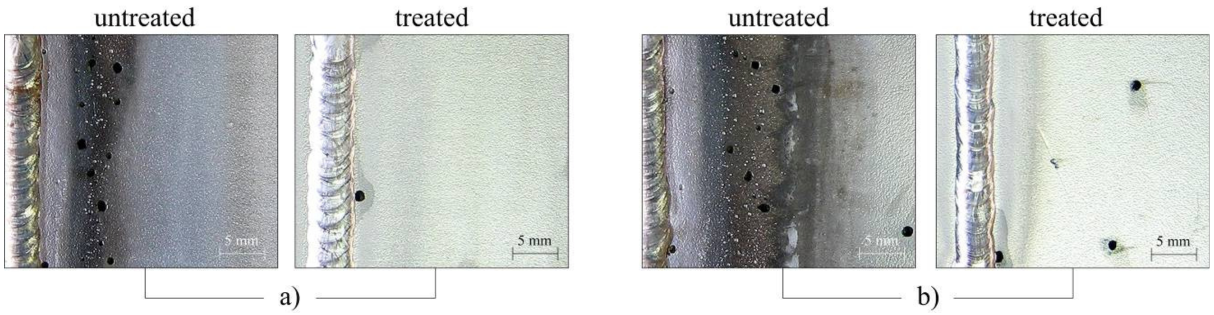


Figure 5. Test results of corrosion resistance of AISI 304L stainless steel after chemical surface treatment: a) "classical" solution 1, b) "environmentally friendlier" solution 1.

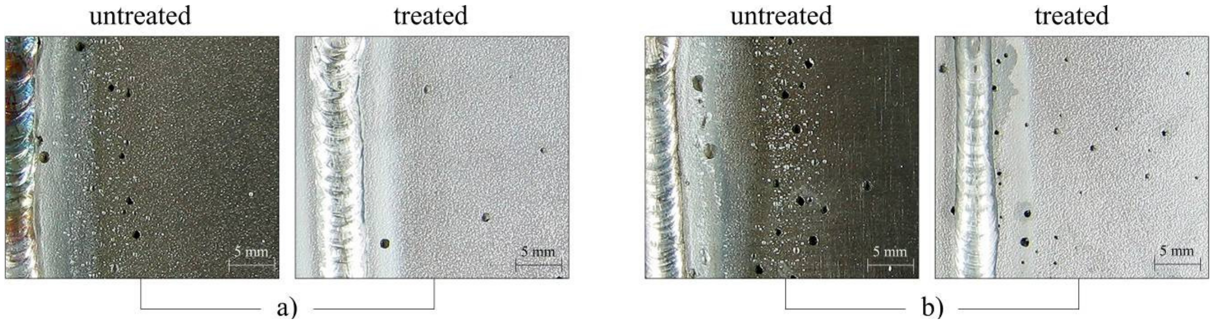


Figure 6. Test results of corrosion resistance of AISI 304L stainless steel after electrochemical surface treatment: a) "classical" solution 2, b) "environmentally friendlier" solution 2.

On samples, on which thermal oxides were not completely removed ("environmentally friendlier" procedures), more intense damage occurred. The test results of resistance towards pitting corrosion are shown in Figures 5 and 6.

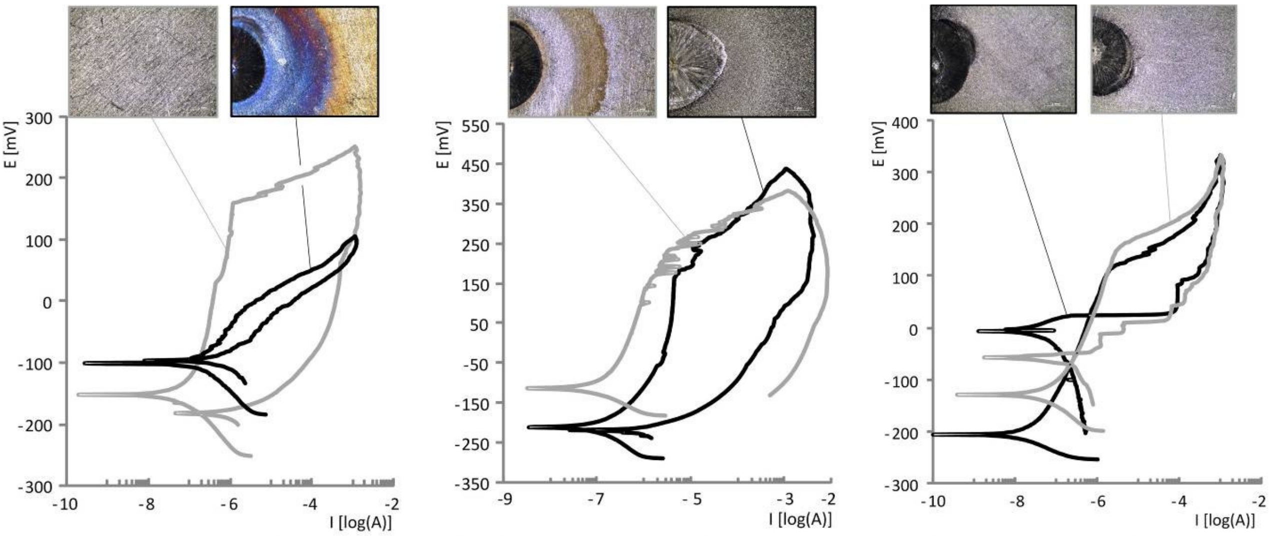
3.2 Testing in accordance with ASTM 61

The results of electrochemical corrosion tests using cyclic polarization are shown in Figure 7, which for better display, gives stereomicroscopic images of the characteristic details of test samples surface before testing.

By analyzing the results, especially taking into account the values of the potential of pitting corrosion (E_{pit}), which represents the potential value at which the passive film under the influence of aggressive ions (predominantly chloride) begins to decline, observed features of the corrosion behavior of test samples are confirmed, ie. the impact of the surface state on the ability to resist corrosion phenomena. It is evident that the untreated sample (with thermal oxides) has no pronounced passive property, but dissolves continuously during the entire process of anodic polarization indicating porosity, as opposed to the base material (the original surface condition) and those samples which have undergone subsequent surface treatment, in which, in a greater or lesser extent, characteristic passivity property was restored and expressed.Also, similarity between corrosion behavior of samples prepared for subsequent surface treatment with "classical" and "environmentally friendlier" solutions can be observed. It is evident that the untreated sample (with thermal oxides) has no pronounced passive property, but dissolves continuously during the entire process of anodic polarization indicating porosity, as opposed to the base material (the original surface condition) and those samples which have undergone subsequent surface treatment, in which, in a greater or lesser extent, characteristic passivity property was restored and expressed.

4 Conclusion

Corrosion resistance of stainless Cr-Ni steels depends significantly on the condition of the surface and the efficiency of the procedures for the removal of thermal oxide. According to ASTM G48 and 61 standards, corrosion resistance test results indicate that in order to restore corrosion resistance, thermal oxides should be completely removed from the surface to allow for passive film formation and maintenance of the unique properties of corrosion resistance that these materials possess, which enables them a wide variety of applications, even in a very aggressive corrosion conditions.



	AISI 304L	E_{pit} [mV]
■	With heat tints	-
▒	Original surface condition	150

	AISI 304L	E_{pit} [mV]
■	"Classical" solution 1	170
▒	"Ecological" solution 1	250

	AISI 304L	E_{pit} [mV]
■	"Classical" solution 2	110
▒	"Ecological" solution 2	150

Figure 7: Diagrams of cyclic polarization for AISI 304L samples in 3.5% NaCl solution.

This comparative study of "classical" and "environmentally friendlier" solutions has shown that the "classical" solutions have greater efficiency in restoration of the passive film, but only in the immersion test. The electrochemical test shows the opposite result. Despite greater efficiency of "classical" solutions, modern "environmentally friendlier" solutions do not fall far behind, and will certainly have a wider use in the future, especially when taking into account the increasingly stringent requirements for environmental protection and professional safety.

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