



Electrochemical characteristics of welded joints on stainless steel in maritime atmosphere

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Abstract: Maritime atmosphere represents the corrosion environment characterized by air saturated with chloride. Many different factors affect the quality of welded joint and the material around it. In case of welding of steel structures, those factors include selection of the welding process, an additional electrode material, and type of lining. Stainless steel is used for different equipment that is exposed to sea water. Connecting those parts together is done by welding method whose quality depends on a number of factors. Some of those factors are investigated in this study. Samples used in experiments are X5CrNi 18-10ASTMAISI304 stainless steel sheets of austenitic type. This sheet is welded in two different ways: manual arc welding in a protective atmosphere of argon and manual arc welding with covered rutile electrode. Corrosion characteristics have been investigated for three distinct zones: zone of welded joint itself, zone in the vicinity of welded joint and zone far from welded joint (basic material). Tests were performed in 0.9% and 3% NaCl solution, as well as in sea water samples from the area of Dubrovnik and Ploče (brackish water). Electrochemical study has been performed by means of potentiodynamic polarization between -0,150 V and 0,350V vs. saturated Ag/AgCl electrode. Results obtained for X5CrNi18-10 austenitic steel and its welded parts in different media at room temperature indicate some degree of self-passivation along with uniform corrosion processes. Based on the obtained results, we concluded that values of corrosion potential lie between 0.350V and -0.150V, depending on the environment in which each sample is probed. In the case of sample welded with dross, increase of corrosion rate does not follow increment of chloride concentration in the expected extent. Corrosion processes are mostly located on the ZUT-OM interface. For the majority of samples, welding in argon atmosphere proved to be a more acceptable way of processing metals from the aspect of corrosion resistance.

INTRODUCTION

Atmospheric corrosion is the most common form of corrosion, and it is defined as the degradation of materials exposed to air and pollution in the air. The most important factor of atmospheric corrosion is appearance of the damp in the form of rain, dew, condensation or high relative air humidity. Corrosion is enhanced by the appearance of dew

and condensation of moisture on the metal surface, especially if they are not followed by frequent washing rains which dilute or eliminate pollutants.

Sea atmosphere, characterized by the air saturated with chloride, represents corrosion environment at sea and near to sea. Sea atmosphere can be extended to a certain distance into continent depending of the topography and dominant wind direction. Depositing particles of sea salt on the metal

surface play an important role in atmospheric corrosion in sea atmosphere. The speed of deposition of NaCl is higher than 15mg/m² daily. Besides that, there are many different chemical loads which make the situation worse, on local level (urban centers, industry etc.). There are studies which examined the corrosion caused by the deposited particles of NaCl, KCl, Na₂SO₄, MgCl₂ i CaCl₂. These salts are also found in sea water and they were identified in sediment on the metal surface (Juraga, Alar, Šimunović, Stojanović, 2007). A thin film of dew, saturated with sea salt or acidic sulfates and acid chloride in an industrial atmosphere, is an aggressive electrolyte that causes corrosion. Wet areas cause condensation of damp on metal surfaces during the night.

Aerosols may occur in two ways: by ejection of particles from the sea surface (sea fog, wind-dispersed dust), or by physical and chemical processes in the atmosphere (secondary aerosols) (<http://www.euro-inox.org>). Stainless steels have become considerably more resistant to aggressive liquids with the growing contents of chromium and molybdenum

Welding is a technological process that forms a monolithic inseparable welded joints by establishing internal connections between particles (atoms, ions, molecules) through local or full heating or plastic deformation or through joint action of both heating and plastic deformation (Pejović, Tomić, Mičić M, Pavlović , 2009).

Electric arc occurs between the work piece and the electrode which can be expendable or inert electrode. In the case of arc welding with protective gas (GMA), the electrode is in the form of wire and metal bath is protected by an inert gas. In case of arc welding by opened arc with covered electrode (SMA), the protective gas is generated by burning the electrode coverings. Trough burning of the cover, dross is formed with a number of additional changes of the area which taken together protect the melt from oxidation. The choice of the electrode is dependable on the types of materials that will be welded and of the welding method. The protective gas is used for majority of welding methods to prevent contamination and oxidation of welded joints, especially for welding of stainless steel, which rapidly oxidized at high temperatures.

The composition of the welded joint included welded seam, zone of base metal with structural and other changes that occurred during the heating (heat-affected zone), and border part of the base metal that has not changed under the welding heat.

Many different factors affect the quality of the weld and materials around it, including the selection of the welding process, the amount and concentration of heat input, weldability of the base material, an additional electrode material, and type of covering, weld geometry and interaction of all these factors.

Heat-affected zone (ZUT) is part of basic material located next to zone of melting. Crystal structure and mechanical properties have been changed by amount of heat introduced by welding in zone of heat impact. Heat-affected zone depends on the heat input and it is usually tight circa 2-8mm. The structure of metal, voltage and thermal gradient change because of the influence of high temperatures in welding processes. Chemical inhomogeneity is often present. Properties of welded joint also depend on the way of welding. Various welding processes produce different microstructures of welded joint and different heat-affected zones. All this factors affect the corrosion behavior of

welded joints (Pejović, Tomić, Mičić, Pavlović, 2009.; <http://www.aston-inox.com>; Pejović B. Tomić, Mičić, 2007). During the welding, partial oxidation often occurs on the surface in the heat-affected zone which is manifested by heat tinting at high temperatures. These oxide films can considerably reduce the corrosion resistance of welded joints so it is necessary to either prevent their formation or remove them if they are formed after welding.

Research objectivities of the present work were: (a) To monitor the corrosion processes occurring on the parts of welded stainless steel; (b) To define types of corrosion attack in certain simulated corrosion conditions; (c) To define the zone in which it corrosion appears in certain corrosion conditions; and (d) To determine the corrosion rate.

EXPERIMENTAL

Material and methods

Samples of stainless steel X5CrNi18-10 ASTM AISI304 of austenitic type are used for the experiments. This sheet was welded in two ways: (a) Manual arc welding in a protective atmosphere of argon, by the electrodes ISO W 19 9 Lsi (Kulušić, Krstulović, Ivić, 2002); (b) Manual arc welding with covered rutile electrode E 19 9 LR 12 (www.pfst.hr/data/materijali/skripta%20Zastita%20materijala.doc). Working electrodes were made according to the sketch in Figure 1 (Kozica, Korać, Cacan, 2011).

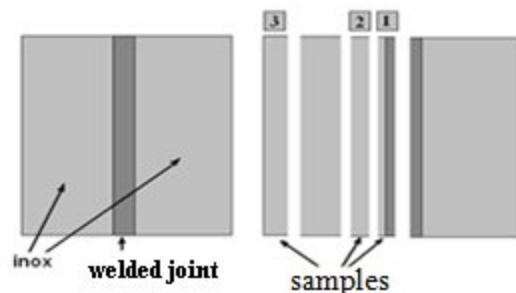


Figure 1: Sketch of the position of samples of working electrodes on the weld.

Sample 1 was cut out so that it includes the border of the weld and metal, sample 2 is a piece of metal close to the weld, and sample 3 was cut out in that way that metal area was 2.5 cm apart from welding. Samples of clean electrodes were also prepared. Dimensions of the electrodes were 2.5 mm × 2 mm. Investigation was done on Potentiostat/Galvanostat 263 A (Princeton Applied Research). Samples of the test material were used as the working electrodes.

As a reference electrode, platinum electrode was placed symmetrically opposed to the working electrode in order for achieving equal distribution of current flux.

All working electrodes were protected by Teflon tape before the start of experiment. The surface of working electrode exposed to solution was defined and the surface was mechanically treated with sand paper of different fineness, from 200 to 1000. Grease was removed from prepared surfaces with ethanol and acetone, and washed with distilled and re-distilled water. Next the surface was activated with a mixture of 30% H₂O₂ and concentrated H₂SO₄ (1:1, v/v) and then washed with distilled water and

re-distilled water. Immediately after the treatment of a surface, the electrode was placed in the prepared electrochemical cell. The corrosion characteristics of already mentioned samples in 0.9% and 3% NaCl solution, as well as in sea water from the area of Dubrovnik and Ploče, Croatia were analyzed. All measurements were conducted at 25±0.5°C.

RESULTS AND DISCUSSION

The values of corrosion potential, corrosion current and calculated corrosion rate were determined from voltammograms presented here (Figure 2 and 3).

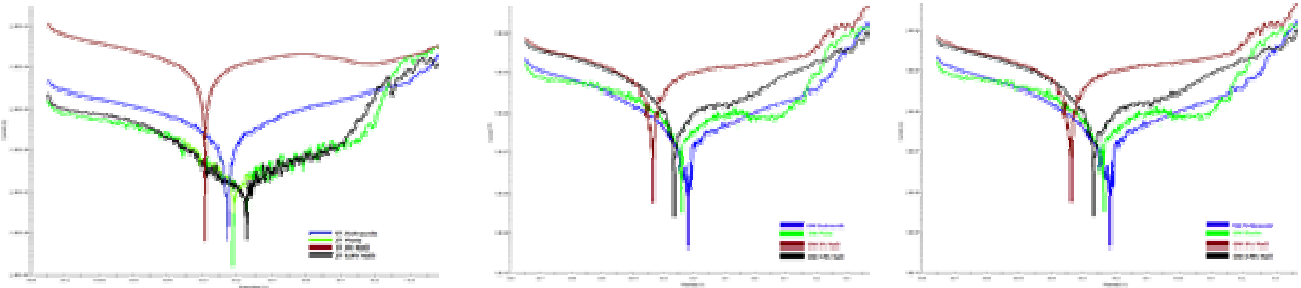


Figure 2. Voltammograms of samples after the welding with argon.

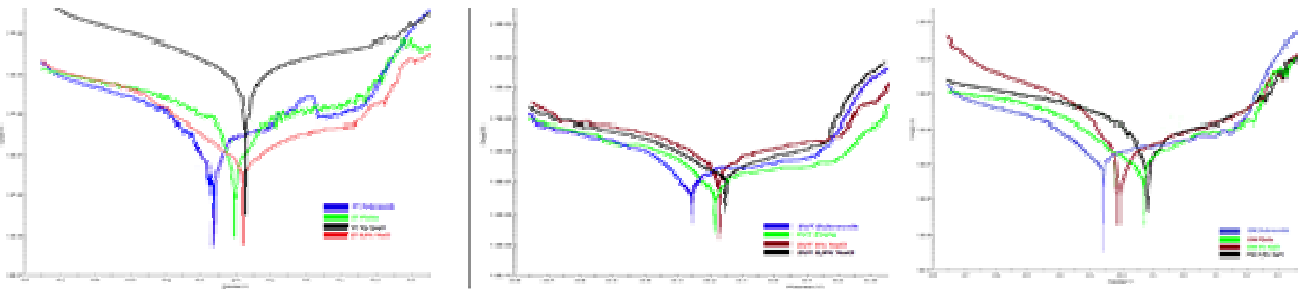


Figure 3. Voltammograms of samples after the welding with dross.

Corrosion potentials (Figure 4), Tafel constants (β_A and β_K) and polarization resistance can be determined from voltammograms obtained by potential-dynamic recordings in different mediums.

Corrosion rate was calculated using the formula:

$$v_{corr} [mm / god] = \frac{0,13 \cdot i_{corr} \cdot M(Fe)}{\rho(Fe) \cdot z} \cdot 25,4$$

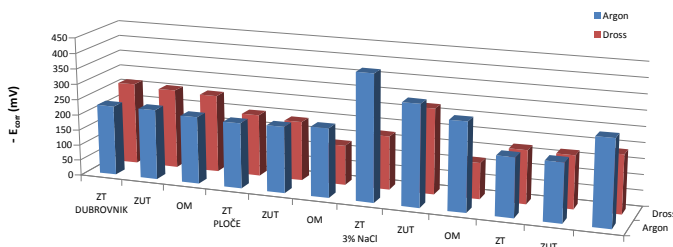


Figure 4. Corrosion potential depending on the sample and ways of welding in different corrosion environments.

Severity of the corrosion current (Figures 5 and 6) was calculated according to the formula:

$$i_{corr} = \frac{\beta_A \cdot \beta_K}{2,3 \cdot (\beta_A + \beta_K)} \cdot \frac{\Delta i}{\Delta E}$$

The highest corrosion instability was found in the sample with heat-affected zone (ZUT) in the case of welding by using dross.

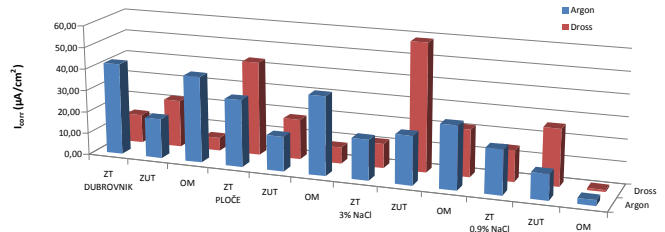


Figure 5. Corrosion current depending on the sample and ways of welding in different corrosion environments.

Expected change of corrosion rate is not present in the case of welding in argon atmosphere, but it can be concluded that melting zone (ZT) suffers heat impact approximately as heat-affected zone (ZUT). The basic material (OM) is generally spared of the corrosive degradation in the case of welding by using dross.

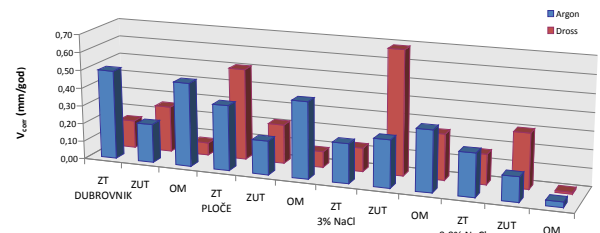


Figure 6. Corrosion rate depending on the sample and ways of welding in different corrosion environments.

Corrosion rate depending on the concentration of chloride ions

Increase in the concentration of chloride ions increases the corrosion rate, which is shown on Figure 7, while the influence of increasing concentrations of chloride is most notable in the sample that represents the base material.

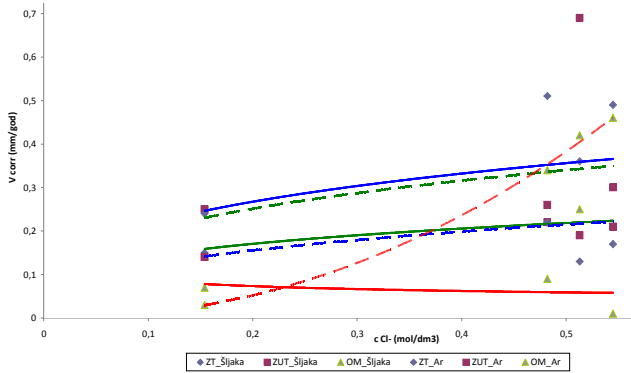


Figure 7. Corrosion rate depending on the concentration of chloride ions.

In the case of samples which are welded with dross, increase in concentration of chloride ions does not follow the expected increase of corrosion rate, so it can be concluded that corrosion in this case is affected by other ions present in water. A sample with heat-affected zone shows the strongest dependence of corrosion rate on chloride ions concentration. Steel plate Samples were tested to check the influence of sea water in coastal areas. Samples surface was mechanically treated with sand paper of different fineness, from 200 to 1000. Grease was removed from prepared surfaces with ethanol and acetone, then washed with distilled water. One sample was exposed to sea water that was in the form of finely dispersed aerosols. Spraying has been performed periodically during the period of four months. The second sample was submerged in 3% NaCl solution for a period of four months. Figures 8 and 9 show layouts of both samples before and after the effects of corrosive medium.

Staining and salt crystals have appeared during the spraying of the first sample with seawater aerosol in a period of 30 days. The next observed change was formation of small, hardly noticeable rust areas, with the characteristic brown-yellow color. The last detected change on metal was formation of small diameter dents and considerable expansion of rust (Figure 8).

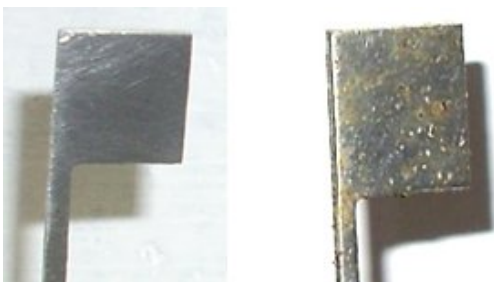


Figure 8. The steel samples sprayed with seawater aerosol.

Sample 2 was kept in the 3% NaCl solution for four months. Formation of coloration on the metal surface appeared first. After a while, the sediment of corrosion

products formed in the beaker where the sample was kept. Three months later, solution has become quite blurred, and any changes on the surface of the sample were difficult to detect. After removing the sample from the beaker, the surface was washed, with distilled water and wiped clean. The large holes on metal were observed that inevitably caused a large mass loss. It is noted that the edges were the most damaged parts, since they served as centers of corrosion (Figure 9).

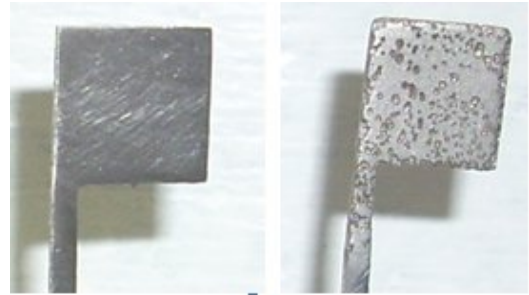


Figure 9. The steel samples submerged in 3% NaCl solution.

CONCLUSIONS

An electrochemical studies of austenitic steel X5CrNi18-10 and its welded parts in different media at room temperature, undoubtedly show that besides corrosive processes, self-passivation processes can occur.

Electrochemical behavior of welded material depends on the chemical stability and condition of the surface, as well as of the thickness and continuity of the formed passive film.

Based on the obtained results it is concluded that the ideal range of working potential varies from 0.350V to -0.150V, depending on the environment in which each sample is located.

Tafel diagrams were recorded in the range from -0.750V to 0.350V, which proved as acceptable because anode part voltamogram in this case is larger and enables making a conclusion about the ability of passivation of metals.

In the case of samples which were welded with dross, increase in concentration of chloride does not follow the expected increase of corrosion rate as expected, so it can be concluded that in this case corrosion affects other ions present in water as well.

Corrosion processes are mostly located on the border between ZUT-OM.

Welding in an atmosphere of argon for the majority of the samples proved as acceptable method of metal processing from the aspect of corrosion resistance.

Samples that represent a basic material, for both types of welding, show more positive corrosion potentials when compared with heat-influence zone and melt zone, also they show lower values of corrosion currents and higher polarization resistance.

The concentrations of chloride ions determined by Mohr method in brackish water from the port of Ploče and seawater from Dubrovnik amounts to 0.482mol/L and 0.513mol/L respectively. Corrosiveness of sea water is proved by the change of the surface sample 1. in experiment of the impact of seawater aerosols.

Corrosion rate increases with the increasing concentration of chloride ions, consequently the material decays faster.

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Summary/Sažetak

Morska atmosfera predstavlja korozionu sredinu koju karakteriše zrak zasićen hloridima. Kod zavarivanja čeličnih konstrukcija mnogo različitih faktora utiče na kvalitet vara i materijala oko njega, uključujući izbor procesa zavarivanja, dodatni materijal elektrode, vrsta obloge. Nehrdajući čelici se koriste za izradu instalacija i uređaja, koji se koriste u morskoj vodi. Spajanje dijelova takvih objekata izvodi se zavarivanjem na čiji kvalitet utiče valiki broj faktora, od kojih su neki istraživani u ovom radu. Za eksperimente su korišteni uzorci inox čeličnog lima X5CrNi18-10 AISI ASTM 304 austenitnog tipa. Ovaj lim je zavarivan na dva načina: ručnim elektrolučnim zavarivanjem u zaštitnoj atmosferi argona i, ručnim elektrolučnim zavarivanjem sa obloženom rutilnom elektrodom. Ispitivane su korozione osobine uzoraka vara, dijela do vara i osnovnog materijala u 0,9% i 3% rastvoru NaCl, kao i u morskoj vodi sa područja Dubrovnika i iz Ploča (bočata voda). Elektrohemijska ispitivanja uzoraka su izvršena potenciodinamičkom polarizacijom od -0,750V do 0,350V u odnosu na zasićenu Ag/AgCl elektrodu. Rezultati ovih ispitivanja austenitnog čelika X5CrNi18-10 i njegovih zavarenih dijelova u različitim medijima na sobnoj temperaturi pokazuju da, pored korozionih procesa, postoje i procesi samopasivacije. Na osnovu dobivenih rezultata se može vidjeti da se vrijednosti korozionih potencijala nalaze između -0,350V i -0,150V, zavisno od sredine u kojoj se pojedini uzorak nalazi. U slučaju uzorka koji je zavarivan sa šljakom porast koncentracije hlorida ne prati brzina korozije u očekivanoj mjeri. Korozijski procesu su pretežno locirani na granici ZUT-OM. Zavarivanje u atmosferi argona se kod većine uzoraka pokazalo kao prihvatljivijim načinom obrade metala s aspekta korozijske postojanosti.