

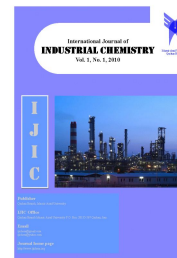


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Electrochemical Study of Welded AISI 304 and 904L Stainless Steel in Seawater in View of Corrosion

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Abstract

This is a comparative study of the corrosion behaviour of welds in AISI 304 and AISI 904L stainless steels carried out in seawater model solution in the temperature range 5-35°C and the standard of corrosion testing of welds was followed. The corrosion rate and corrosion attack characteristics were determined for welds of the examined steels with several type of treatment. The aim of this work was to compare the steels based on their resistance against the corrosion in terms of pitting potential (E_{pit}) and repassivation potential (E_{repass}). Seawater is an electrochemically aggressive medium, which can initiate localised corrosion in welded stainless steels. Different electrochemical and testing methods were used, including cyclic voltammetry, chronopotentiometry, electrochemical impedance spectroscopy (EIS), pH measuring and penetration tests.

Keywords: AISI 304; AISI 904L; Pitting corrosion; Seawater; Weld

1. Introduction

Alloys used for submarine operation should resist corrosion and other destructive processes, caused by the aggressive environment. Containers, pipelines and several type of tanks should be resistant against corrosion for isolating the inner material from the surroundings. The examined steels were AISI 904L type stainless steel and AISI 304 the latter is often used as structural material for pump houses and for desalination plants, as well as in different parts of submarines. Several

breakdowns occurred caused by the localized corrosion of AISI 304 alloy initiated by the chloride content of the seawater. Studies are published mostly about the corrosion of the AISI 304 and despite of all efforts no proper replacement has been found for this alloy for submarine applications. AISI 904L type stainless steel should be more resistive against the corrosion due to the significantly lower iron and higher Ni content but there is no study about this alloy and its behaviour in brine. This

steel could be a good alternative to replace the AISI 304 steel where corrosion and chemical resistance required. In general several studies dealt with the issue of the corrosion behaviour of steels, but no one studied the welds. The usual approach is that corrosion is studied at well defined and well known inorganic acid solutions [1,2]. Nowadays significant amount of empirical data and information has been accumulated about the effect of chloride on corrosion of some technically important steels. Some papers are dealing with the corrosion problems in seawater in flowing condition [3-7]. Some of the studies are electrochemical one, and focusing to the modification of the AISI 304 stainless steel surface to improve corrosion resistance [8,9].

Melchers et al [10] interpreted the long-term corrosion of chromium steels in seawater and give a model for the corrosion process. The influence of bacteria activity in corrosion is examined also. Lots of papers are about corrosion of steels in seawater [11-13], but none of them mentioned the corrosion of the welds. Melchers [14] investigated the pit depth on high strength low alloys in seawater and made extrapolation for larger areas and long-term exposures.

Studies concerning the corrosion resistance of welded steels are very rare. Garcia-Garcia, Blasco-Tamarit et al [15,16] studied the corrosion of high alloyed austenitic stainless steels and their welds but in LiBr environment. They compared the corrosion behaviour of two type of welded steel in lithium bromide solution by using electrochemical methods. Not only is the corrosion behaviour of the steels interesting in seawater but their welds also. (deleted)

However AISI 304 is an inexpensive and commercial steel, but the replacement is expensive enough to motivate us to search an alternative for replacing.

This paper presents the required measurements and results about behaviour of the welds of AISI 304 and 904L type stainless

steels under marine conditions. Temperature is an important factor influencing the corrosion of austenitic stainless steels [17,18] that is the reason why we extended the studied temperature range to 5-35°C, which covers the whole natural seawater temperature range. The importance of the experiments is confirmed by the fact that the composition of the groundwater can be similar to the seawater. Pumps of thermal water or structural materials used for getting geothermal energy can be in a huge corrosion hazard. The environment under 600 m depth is like single phase high salinity brine.

The different results between the two alloys can be guaranteed from their composition, but weldment can modify and weaken the structure and literature does not give answer to the uncertainty of it. The main aim was to see the difference between the corrosion behaviour of the alloys after welding. We used the ASTM G48 standard (the corrosion testing of welds standard) to categorise the welded alloys.

2. Experimental

2. 1. Metals

Two types of austenitic stainless steel were examined; AISI 304 (1.4301) and AISI 904L (1.4539). The compositions of these steels are summarized in Table 1, data were measured by EDAX (Philips XL 30 Series, EDAX Detecting Unit). According to the literature the carbon content was 0.08 % in AISI 304 and it was 0.02 % in case of the AISI 904L type steel.

On the surface of AISI 304 stainless steel sample small inclusions were found which provided us an opportunity to examine the composition of the surface impurities. Inclusions can be formed during the rolling or forging process and they have an important role in the crevice chemistry. When these impurities getting out to the surface localised corrosion can be initiated [19]. Inside the inclusion sulphur concentrated in the form of MnS (Fig. 1.). Sulphur-containing inclusions in AISI 304

steel were studied by Daufin [20], his study was used for understanding the role of impurities containing MnS.

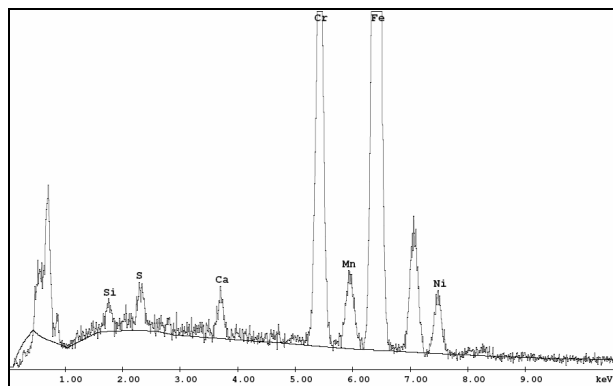


Fig. 1. Experimental determination of the composition of the inclusion by EDAX

Inclusions are important from the point of pitting as they can initiate this process by dissolving in the electrolyte leaving a hole unlikely to repassivate because of its openness. Pitting also can be induced by dissolving the matrix around the inclusions, where crevice can appear. In this acidic condition prevailing inside the crack due to the hydrolysis of anodically dissolved metal ions. The MnS inclusions act as local cathodes and H₂S is formed on them.

Studies were extended to several kinds of welded samples, with or without polished surface and two of them had electro-polished welds. Unwelded samples were used for reference.

For giving the difference of pitting resistance between the alloys, PREN (Pitting Resistance Equivalent) was determined. The

calculation based on the chemical content of the alloy, but the result has no dimension so it is used only for comparing steels.

$$PREN = Cr + 3.3Mo + 16N$$

Where Cr, Mo and N are the mass percent from the EDAX measurements. Nitrogen was calculated from standard data. For AISI 304 PREN was 18.16 and for AISI 904L steel it was 32.81.

2. 2. Welding parameters

During the stud welding process (62 A, 0.07 s) argon plasma was used to avoid contamination by other metals. (The possibility of galvanic corrosion must be considered if stainless steel is used in contact with other metals in seawater.) Due to the welding the texture of the metal changes, some impurities could melt into the weld, and due to the heat the surface structure also changes. These problems could increase the sensitivity against localised corrosion. On Fig. 2 some microscope photos are shown about intersects of the weld.

Polishing was necessary for removing the impurities concentrated into the weld and on the surface of the alloys. Impurities usually stuck into the weld because this part of the metal cools down at last. The used instruments were Saint-Gobain Abrasives A/S 508242 polishing disk and NITTY-GRITTY S.R.I./TIG. CLINOX PRO equipment for electro-polishing. The geometry of the used samples was 1 mm thick plates of 10x10mm (masked to 2x5mm before using).

Table 1. Experimentally determined composition of the steels

Steel	Mass %									
	% Fe	% Si	% Mn	% Cr	% Cu	% Mo	% Ni	% P	% S	% N
AISI 304	(71.06) balanced	0.63	1.54	18.16	-	-	8.42	0.19	-	-
AISI 904L	(48.20) balanced	0.45	1.44	19.51	1.98	4.03	24.40	-	-	-
AISI 304 Small inclusion	(70.52) balanced	0.80	-	18.91	-	1.16	6.41	1.06	1.16	-

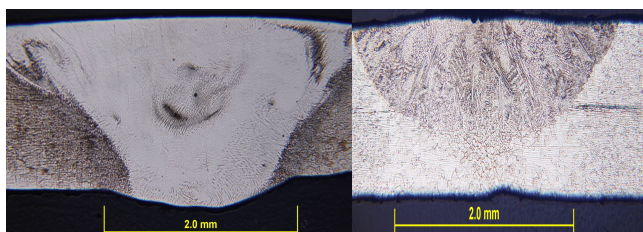


Fig. 2. a- welded AISI 304; b- welded AISI 904L alloy, neither of them polished

2. 3. Solutions

Seawater model was prepared by the ASTM D1141 Standard. The salt contents of the artificial seawater were: 24.53 g/L NaCl, 5.2 g/L MgCl₂, 4.09 g/L Na₂SO₄, 1.15 g/L CaCl₂, 0.695 g/L KCl, 0.168 g/L NaHCO₃. All chemicals were analytical purity (Sigma-Aldrich). The pH was 8,96 on 25°C. To decrease the initial oxygen content of the solution argon was used for de-aeration. In this study the corrosion testing of welds standard (ASTM G48) was followed. The chronopotentiometric measurements were carried out at zero current in aqueous FeCl₃ solution. 100 g FeCl₃·6H₂O were dissolved in 900 g double distilled water and the pH of the solution was 1.5L at 25°C. This solution was used for soaking the alloy samples also.

For the pH measurements, CONSORT C830 equipment with a pH sensitive glass electrode and a saturated calomel electrode was used in thermostated solution.

3. Results and Discussion

Investigations on pitting corrosion of stainless steels are mostly performed by electrochemical techniques, because in this way the pitting potential, the repassivation potential or the critical pitting temperature - quantities characterizing the corrosion process - can be determined. Impedance measurements were performed to determine the basic differences between the two steels.

3. 1. Cyclic voltammetry

Cyclic voltammogram (CV) is widely used for defining the pitting potential and describing the charge-transfer reactions on the metal

surface and determine the presence and the behaviour of the oxide layer. Due to the welding process, the texture of the surface changed, the grains coarsened. According to the results all of them enhance the sensitivity of the weld and its vicinity against the localised corrosion.

Measurements were carried out in a thermostated glass cell which provides us the constant temperature (5°C, 15°C, 25°C and 35°C) with a EF453 type PC controlled potentiostat. The solution was artificial seawater which was de-aerated with argon. Working electrode was the sample under test (2x5mm), there was a platinum mesh as a counter electrode and the reference was a saturated calomel electrode (SCE) connected by a Luggin-capillary. The recorded potential cycle was from -900 mV to 200 mV and the used scan rate was 5 mV/s; during the potential sweep the current was recorded. The initial value of the CV (-900mV) was the open circuit potential. Ethanol and distilled water rinse were applied for preparing a chemically clean surface. None of the measurements at 5°C shows any sign of corrosion. The experimental data (cyclic voltammogram) were analyzed by linear fitting to determine the pitting potential (E_{pit}) and the repassivation potential (E_{repass}). On the first scans of the CVs much higher current were found caused by desorption or dissolution of the impurities and the expansion of the oxide layer on the metal surface, therefore the second scans were used to determine the critical potentials. The measuring results are shown on Fig. 3.

With increasing temperature the anodic current increased and E_{pit} with E_{repass} decreased and drifted to the higher negative (cathodic) region. Due to this drifting the oxide layer grew and the steel become more resistant; according to the third scan a strong passive layer has grown and the charge-transfer reaction decreased as the falling current shows. Generally speaking, the individual samples became more resistant during the scanning at

low temperature. In case of the experimental series the intensity of the corrosion attack increased with the increases in temperature. At anodic potential the noise of the current appeared caused by the pitting corrosion. The high current value - at anodic potential - indicates the dissolution of the metal from the surface[21]. The current noise on the CV marked the presence of pitting, while the flat curve indicates the capacity of the double layer and the oxide layer and the lack of pitting. Summarizing the results; at low temperature all type of steels and welds remained resistant against the pitting and a constant oxide layer grew on the surface.

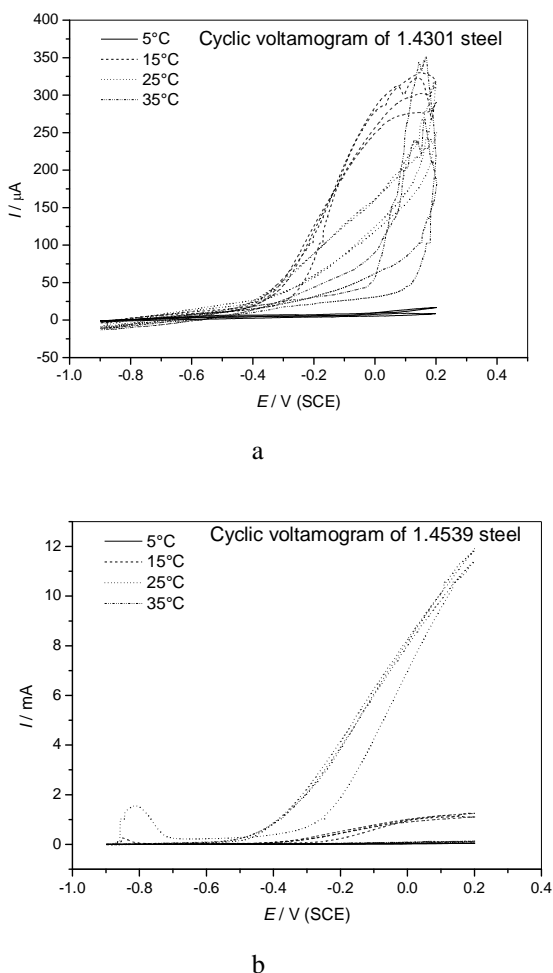


Fig. 3. Cyclic voltammograms (CVs) of the (a) 1.4301 (AISI 304) and (b) 1.4539 (AISI 904L) type stainless steels at various temperatures, scan rate 5 mV/s.

With increasing temperature on the weldment – without pre-treatment – wide pits grew which meant fast iron dissolution. Pre-treatment, polishing and electro-polishing removed the impurities which can dissolved first in seawater leaving a hole behind where solution can initiate. Corrosion resistivity of weldment can be improved by electro polishing.

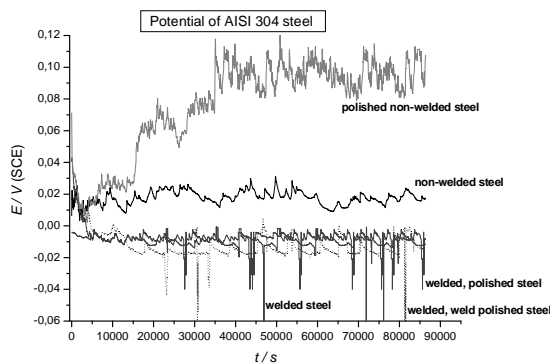
3. 2. Chronopotentiometry

The aim of this measurement was to determine the open circuit potential (with zero current) of the alloys. The base solution contained proper amount of FeCl_3 (mentioned before). We followed the corrosion testing of welds standard (ASTM G48) and recorded the change of the potential 24 hours long. The potential noise belongs to oxidation/reduction of the iron from/to the surface [21,22]. At the end of the 24 hour measurement the potential should reach a stationery value. The experimental data are shown on Fig. 4.

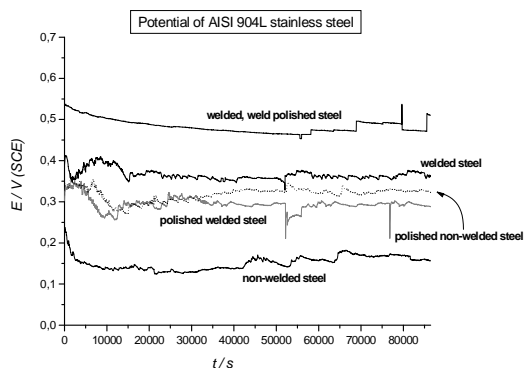
In case of AISI 904L type steel no sign of charge transfer reactions was obtained because of the passive oxide layer, unlike on AISI 304 where – as it is shown on Fig. 4 several potential peaks caused by the pitting appeared. In case of AISI 304 steel weldment procedure shifted the potential of the samples to more negative range and set it to the same value about -0.01 V. In case of the other type of steel every sample had their own potential, which was different for all of the electrodes and only a slight fluctuation occurred.

3. 3. Electrochemical Impedance Spectroscopy (EIS)

The aim of this type of measurements was to determine the basic differences between the two steels, and to give estimation to the rate of corrosion. The measured spectra are on Fig. 5 and Fig. 6. The differences in the spectra are visible in both representations.



a

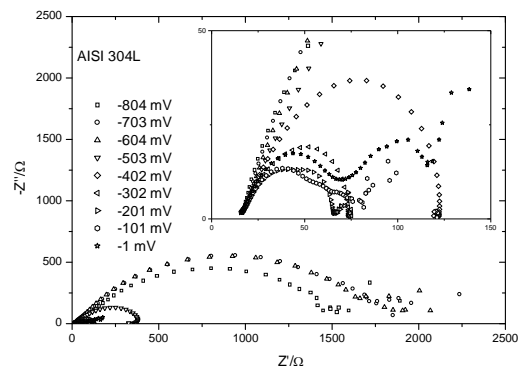


b

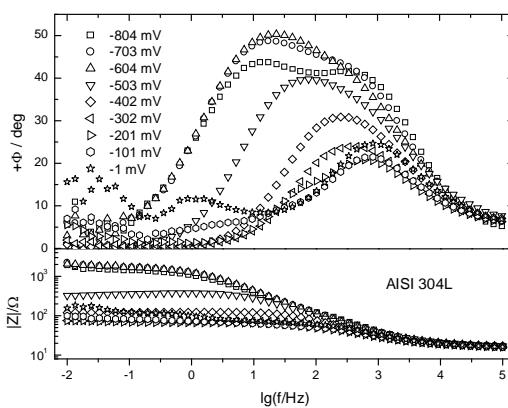
Fig. 4. Open circuit potentials (OCPs) of the AISI 304 (a) and 904L type stainless steels (b) at 20°C.

Faraday model can be fitted on the spectra of the AISI 904L samples. The protective oxide layer behaves as a capacitance. In case of AISI 904L the impedance (measured at low and high frequencies) are 3 orders of magnitude higher than in case of AISI 304 samples. The impedance in low frequency - which includes among others the solution resistance - is high due to the high resistance of the oxide layer. The high value of the impedance in high frequency comes from the passive state. The measured impedance in high frequency characterizes the rate of the processes on the steel. Due to the higher impedance the rate of the processes on AISI 904L samples is thousand times slower than on AISI 304 steel.

Without a preliminary model no equivalent circuit can be determined for the spectra of the



a



b

Fig. 5. (a) Argand plot, (b) Bode plot of EIS on AISI 304

AISI 304L samples. In case of steels hard to forecast all of the processes take on the surface. Despite the lack of knowledge of the electrochemical and chemical reactions, the differences between the two steels are noticeable and show remarkable change in the passivity.

3. 4. Soaking and penetration

Both metals were soaked 48 hours in FeCl₃ solution in the same concentration used in case of chronopotentiometry. After rinsing and drying, penetration was taken. All metal samples were measured before and after soaking and mass decrease was obtained at all samples. The penetration substance makes the corrosion traces visible. Fig. 7 shows the AISI 304 samples and Fig. 8 shows the AISI 904L samples after soaking.

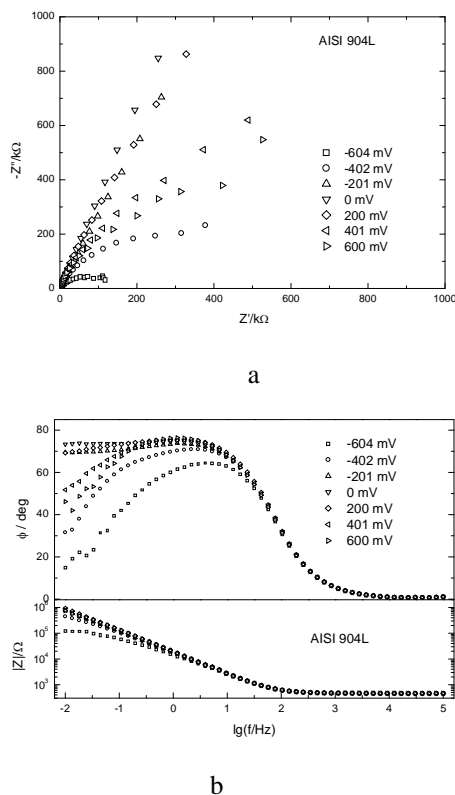


Fig. 6. (a) Argand plot; (b) Bode plot of EIS on AISI 904L

In case of AISI 304 pits appeared on the surface of the samples in positions depending on the pre-treatment. In case of welded, non-polished steel, pits opened up on the region of the weld and the heat affected zone (HAZ). On the polished, welded sample pits appeared only on the weld, but in case of the electro polished surface no pits were observed. On the non-welded, unpolished steel – reference sample - localised corrosion was found everywhere without an arbitrary position and on the surface of the polished non-welded steel some pits developed on the edge of the plate.

We can conclude that polishing can increase the resistance against the localised corrosion, by removing impurities melted into the welded region. After polishing a new passive oxide layer grew on the metal surface without contamination.

In case of AISI 904L few pits developed in one of the sample, the others resisted the attack of chloride. On the welded non polished metal surface, a small number of pits were found

probably caused by the lack of the surface treatment. Welding procedure damaged the passive oxide layer and heat might cause changes in the texture of the steel, the grains melted and the crystal structure changed.

4. Conclusions

AISI 304 and 904L type austenitic stainless steels with different treatment/history (welded/un-welded/polished/unpolished) were studied in seawater at several temperatures by electrochemical methods. Experimental results show significant differences between the studied steels. In case of AISI 304 the high mass percent of iron makes the alloy sensitive for localised corrosion, while in case of 904L steel the low iron content with the high mass percent of Ni and Cr enhance the corrosion resistance. Both steels have low carbon content. At higher temperature, the chloride content of the artificial seawater became more aggressive and attacked the metal surface and the anodic current increased (faster oxidation) while the appeared current noise shows evidence of pitting corrosion. AISI 304 type steel had sulphurous inclusions on the surface – due to the preparing procedure - making the resistance of the region electrochemically weaker and the surroundings of the inclusion vulnerable. In case of AISI 904L type alloy we did not find any inclusions (sulphur) on the surface therefore it can resist localised corrosion. By polishing the weld, inclusions and some impurities on the surface removed and with this the corrosion resistance can be improved. In case of soaking experiments some of the AISI 304 type steel samples perforated in the whole depth at the welding and the region of the heat affecting zone. Welding process makes the alloys more vulnerable, due to the surface recrystallisation and molten-in impurities. Due to the high Ni (24.40) and Mo (4.03) and low carbon content, the AISI 904L type austenitic stainless steel resists to corrosion.

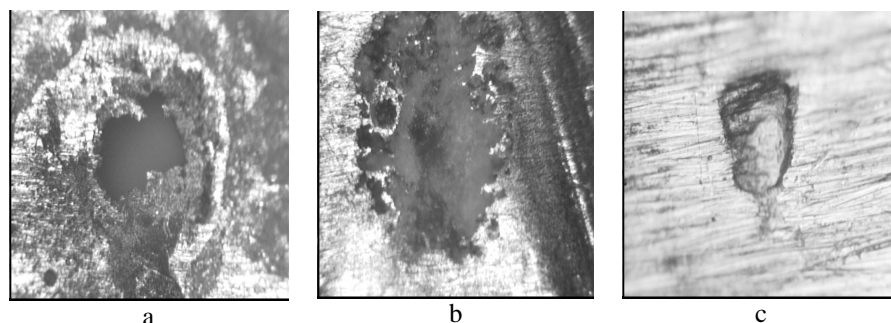


Fig. 7. (a) non-welded non-polished steel plate; (b) welded non-polished steel; (c) welded polished AISI 304L steel sample (Olympus B071 type microscope 1mm x 1mm)

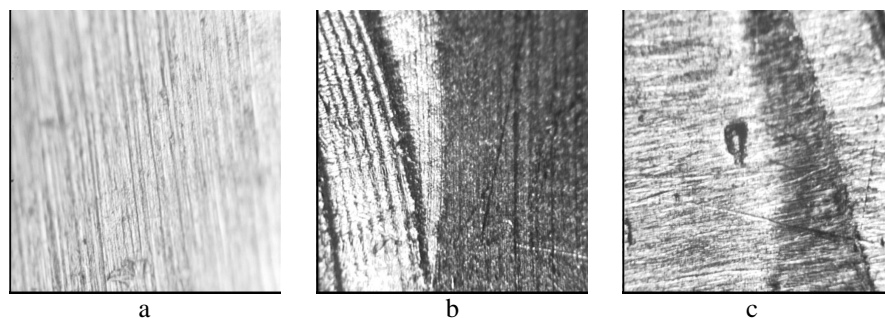


Fig. 8. (a) non-welded and non-polished steel plate; (b) welded and polished steel; (c) welded and non-polished 904L steel sample (Olympus B071 type microscope 1mm x 1mm)

The aim of the work was to find an alloy which can replace the AISI 304 type steel at submarine operation with high resistance against localised corrosion along the welds. AISI 904L type stainless steel can be a good candidate to solve this corrosion problem.

Acknowledgement

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