SURFACE STATE EFFECT OF WELDED STAINLESS STEELS ON CORROSION BEHAVIOR

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Abstract
Welding joints of stainless steels are in practice very sensitive places attacked by local corrosion, such as pitting and crevice corrosion, mostly in chloride containing oxidizing environments. It is caused by different oxidation products created on the surface by welding. Corrosion resistance of stainless steels is affected by quality of passive layer (Cr_2O_3) which created at normal conditions on air. After welding the steels are heated and on the surface are originated different types of oxides which have not the same protective properties. Resistances to intercrystalline and pitting corrosion of two type of welded stainless steel with different surface finishing were tested. Experimental materials are the austenitic stainless steel AISI 316L (welded by the TIG method in inert Ar atmosphere with filler) and the ferritic stainless steel AISI CA6-NM (welded by the WPS method in inert Ar atmosphere with filler and after welding heat treated). Character of the surface after welding and after mechanical finishing by grinding was evaluated by SEM microscopy, EDX analysis. Corrosion resistance to local forms of corrosion was tested by electrochemical potentiodynamic test and by exposure tests in chloride solutions. The steel AISI CA6-NM was tested in fluvial water to simulate real operation environment. The evaluation is supported by microscopic analysis. Susceptibility to intergranular corrosion was tested too and results detect the dangerous localities for corrosion attack and show increasing of corrosion resistance by surface treatment.

Keywords: weld joint, stainless steel, surface, corrosion resistance

1 Introduction

Stainless steels are considered corrosion resistant construction material. Corrosion stability is because of creation of a passive layer on surface at normal conditions on air. Welding joints of them are in practice very sensitive places attacked by local corrosion, such as pitting and crevice corrosion, mostly in chloride containing oxidizing environments. Initiation of the mentioned forms of local corrosion occurs when chloride ions concentration in solution exceeds a critical value. This value depends principally on materials properties (composition, deformation degree, heat treatment, surface finishing) and environment properties (temperature, pH, presence of oxidizing environment, flow regime). The behavior of stainless steels with respect to pitting or crevice corrosion has been studied extensively by many authors over the last 50 years on the

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basis of different laboratory approaches [1-7]. Welding of stainless steels is carried out at high temperature and it affects their corrosion resistance by microsegregation, precipitation of secondary phases, formation of unmixed zones, recrystallization and grain growth in the weld heat-affected zone (HAZ), residual welding flux, microfissures, beginning or end of weld passes creating crevices, presence of "heat tinted oxides" formed on the surface.
The region near the surface of an oxidized stainless steel is depleted in one or more of the elements that have reacted with the surrounding atmosphere. The oxidized, or heat-tinted, surface of a welded stainless steel consists of a heterogeneous oxide composed primarily of iron and chromium above a chromium-depleted layer of base metal. A heat-tint oxide on an austenitic stainless steel exposed in air appears at approximately 400 °C. As the surface temperature is increased, differently colored oxides develop. Dark blue heat-tint oxides are known as the most susceptible to localized corrosion. The undesired oxides are created on the surface of stainless steel after heat treatment too [8-16].
In our research work the influence of various surface treatments (mechanical and chemical) of the stainless steel is dealt with. In this publication only a part of results will be presented to show high effect of surface state on corrosion behavior.

2 Experiments and results

2.1 Characterization of experimental materials and surfaces

Resistance to intercrystaline and pitting corrosion of two type of welded stainless steel with different surface condition were tested. Experimental materials are the austenitic stainless steel AISI 316L and the ferritic stainless steel AISI CA6-NM with chemical composition listed in **Table 1**.
The steel AISI 316L was welded by the TIG method in inert argon atmosphere with filler of the same chemical composition. The steel AISI CA6-NM was welded by the WPS method with filler. This steel was after welding heat treated (preheating to temperature 150°C, cooling was made in wrap; heating to temperature 600°C, holding time for 2 hours, cooling in a furnace at temperature 150°C, cooling in air).

Table 1 Chemical composition of the experimental stainless steels

Elements/wg.%	**Cr**	**Ni**	**Mo**	**Mn**	**C**	**Si**	**N**	**P**	**S**	**Fe**
AISI 316L	16.51	10.21	2.10	0.91	0.013	0.65	0.015	0.038	0.006	balance
AISI CA6-NM	12.8	3.7	0.49	0.65	0.029	0.32	0.029	0.014	0.011	balance

The microstructure of base material (BM), heat affected zone (HAZ) and weld metal (WM) were studied by metallography and they are given in **Fig. 1**. In heat affected zones and in weld metal no defects are observed.
The corrosion tests were made on specimens without surface finishing and after finishing of welded specimen by grinding. The specimens after welding are shown in **Fig. 2**.
Initial surface grinding of the specimen AISI 316L was performed to level up the surface of the welded area with base material. This was done by using surface grinding with Al_2O_3 belt with grit of 80. Then each specimen was grinded by Al_2O_3 belt with grit of 180 for 3-4 minutes. The changes of chemical composition of the unfinished (**Fig. 3**) and ground (**Fig. 4**) surfaces are in

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Table 2. By grounding undesirable oxides were removed of the surface and the roughness was changed too.

BM HAZ WM

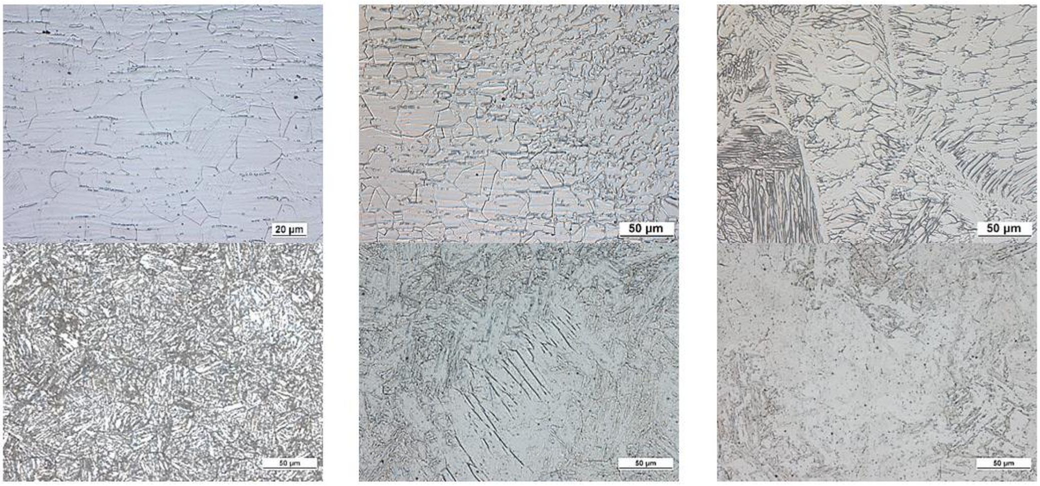


Fig. 1 Microstructure of the base metal, heat affected zone and weld metal after heat treatment of the steels AISI 316L (upper row) and AISI CA6-NM (lower row)

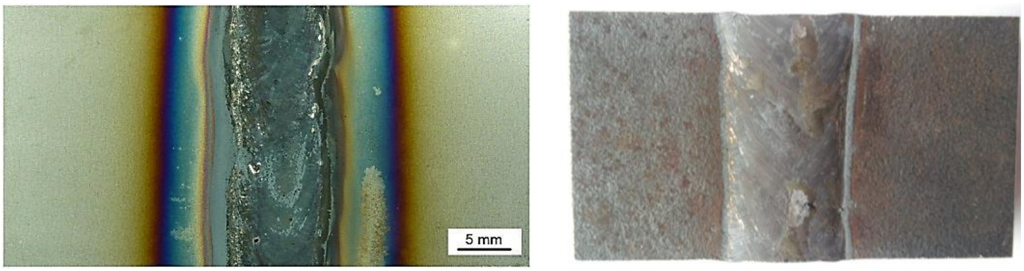
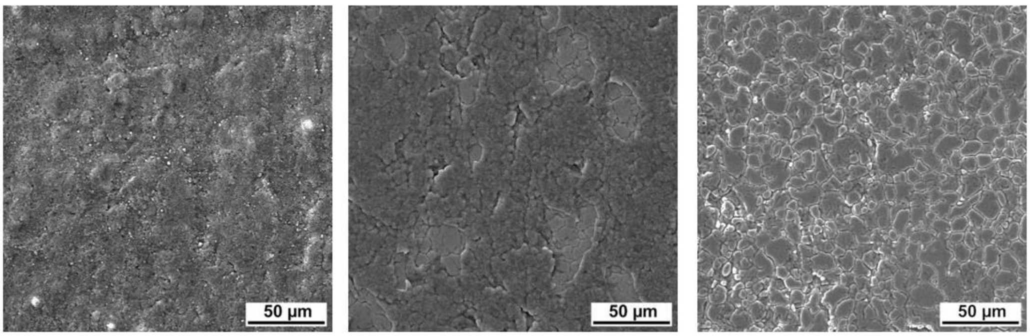


Fig. 2 Surface of the specimens after welding (AISI 316L)and heat treatment (AISI CA6-NM)



BM **HAZ** **WM**

Fig. 3 EDX analysis of the unfinished welded specimen

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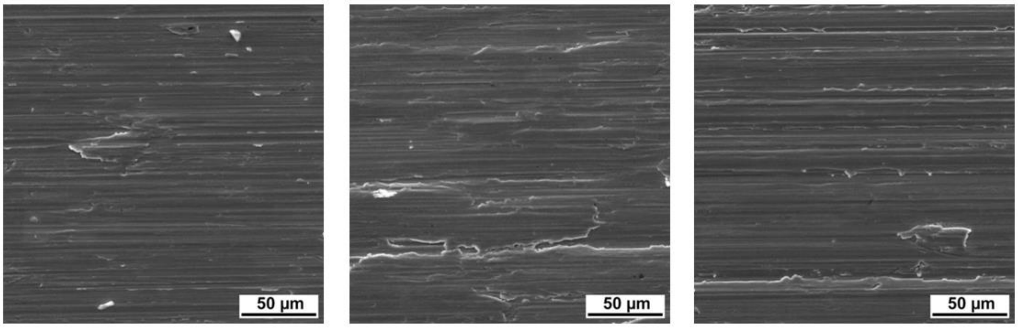

BM **HAZ** **WM**

Fig. 4 EDX analysis of the unfinished welded specimen

Table 2 EDX analyses of the no treated and ground surfaces of welding AISI 316L

		Elements (wg. %)						
		O	**Si**	**S**	**Cr**	**Fe**	**Ni**	**Mo**
Weld joint of AISI 316L unfinished	*WM*	24.22	0.85	0.02	16.10	33.53	12.43	1.94
	HAZ	5.88	0.33	0.00	13.91	62.46	8.47	2.12
	BM	0.29	0.43	0.11	14.71	66.79	9.8	2.07
		Elements (wg. %)						
		O	**Si**	**S**	**Cr**	**Fe**	**Ni**	**Mo**
Weld joint of AISI 316L ground	*WM*	0.52	0.47	0.06	14.97	67.21	9.11	2.14
	HAZ	0.29	0.43	0.00	15.36	66.01	9.29	2.34
	BM	0.56	0.36	0.08	15.,23	66.89	9.45	2.05

2.2 Corrosion tests

Corrosion properties of the welded steels were studied by potentiodynamic and Stauss´ tests and by gravimetric analysis the AISI 316L.

Gravimetric analysis

Resistance to pitting corrosion of the AISI 316L welded specimens with diverse surface state was tested by immersion test using the 6% of $FeCl_3$ solution (according to the standard ASTM G 48) [17]. The environment temperature during the experiment was 21 °C. After exposition in the test solution (72 hours) the specimens were cleaned and dried, weighted on an analytical balance with the accuracy of 10^{-5} g and the corrosion rates were calculated. Results of are listed in Table 3 and it is apparently observed the effect of surface treatment.

Table 3 Corrosion rates of the AISI 316L stainless steel in 6% $FeCl_3$ solution

Type of surface treatment	Average weight losses [g]	Average corrosion rates [$g \times m^{-2} \times h^{-1}$]
Unfinished	0.30041	3.33788
Ground finish	0.28217	3.13522

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Potentiodynamic polarization tests

Cyclic potentiodynamic polarization studies were made with a three-electrode system using a computer-controlled potentiostate/galvanostate VSP (Biologic) with the power Sorens SGA (ASTM G5 Standard reference Test Method for Making Potentiostatic and Anodic Polarization measurement) [18].The tests were performed in locality of base material and weld metal. The open surface was 0,5 cm^2 and the measuring was realized versus saturated calomel electrode (SCE) as reference electrode and platinum electrode as counter electrode. All experiments were made at 25±1°C, in the range -400 mV +400 mV vs. E_{oc}, setting delay was 10 minutes and the scan rate was 1 mV/s. By this method characteristic potentials of pitting were measured (E_{dp} – depasivation potential (breakdown) and E_{rp} – repasivation potential) for base metal and weld metal. The testing environmentwas the 3.5% solution of NaCl. According to the results shown in **Table 4** grinding does not change depasivation potential of basic material but its difference in weld metal was evident.

Table 4 Potential E_{dp} of no treated and ground surfaces of the welded AISI 316L

Potentials of BM	***Unfinished***	***Ground***	Potentials of WM	***Unfinished***	***Ground***
E_{dp} (mV)	385	268	**E_{dp} (mV)**	- 94	140
E_{rp} (mV)	-137	-193	**E_{rp} (mV)**	-242	-180

The solution for the AISI CA6-MN was natural water modified to value pH 5 by addition of HCl, (increasing of chlorides was negligible (0.036g Cl^- in one dm^{3}of water). Environment was selected according to supposed working conditions (water turbine vane). Electrochemical characteristics (Corrosion potential; corrosion current density and corrosion rate) were determined using the Tafel extrapolation method. The comparison of representative corrosion parameters are cited in **Table 5** and **Fig. 5**.

Table 5 Results of potentiodynamic tests measured on unfinished and finished surface

AISI CA6-NM	**E_{corr} [mV]**	**i_{corr} [μA.cm^{-2}]**	**b_c [mV]**	**b_a [mV]**	**v_{corr} [mm.year^{-1}]**
	Unfinished surface after welding				
BM	-343.141	5.561	426.6	230.1	0.258
WM	-384.197	1.588	313.6	188.7	0.073
	Finished surface				
BM	-217.231	0.797	293.1	321.5	0.037
WM	-230.417	0.889	277.2	258.0	0.041

The corrosion characteristics measured on the evidently oxidized surface and finishedsurface are different, what confirmed strong influence of surface treatment after heat affecting of stainless steels. Corrosion potential of clean surfaces is above 120 mV more noble than the oxidize ones on base metal and in WM is difference higher. Corrosion rate of BM with clean surface is low order beside oxidized one. Differences of corrosion rates measured in weld metal are of finished surface less too (**Table 5**).

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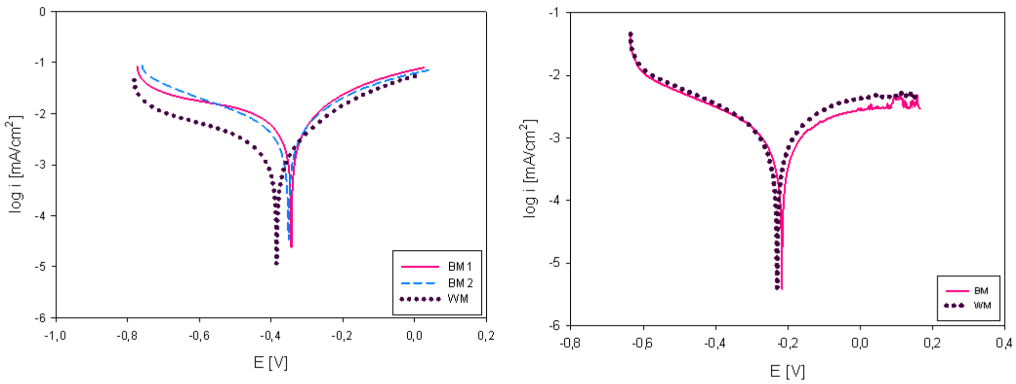

Fig. 5 Course of potentiodynamic curves of BM and WM on unfinished and finished surfaces

Test of susceptibility to intercrystalline corrosion

Unsuitable surface state can increase susceptibility of stainless steels to intercrystalline attack [19-21]. Sensitivity to intercrystalline corrosion was tested for both welded materials. Experiments were carried out according to the standard STN EN ISO 3651-2 in the solution of $CuSO_4$, H_2SO_4 and water (Strauss´ test) lasted 24 hour [22]. The results are presented in **Fig. 6** and **7**.

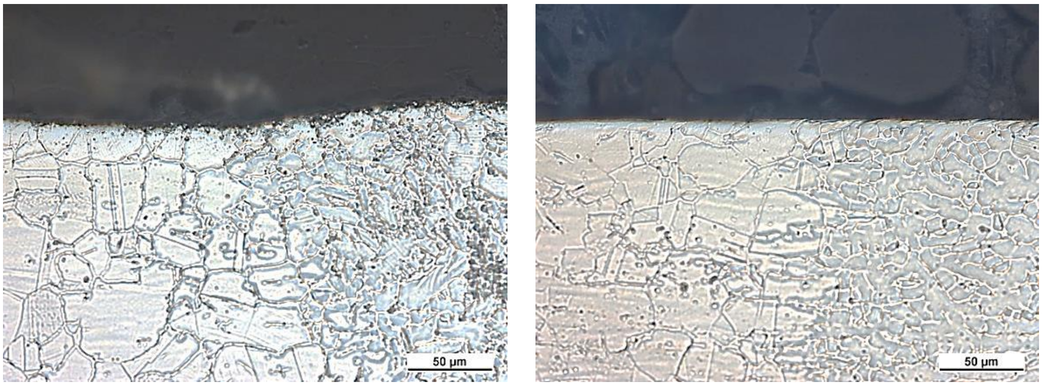

Fig. 6 Unfinished and ground specimens of the AISI 316L after Srtauss´test

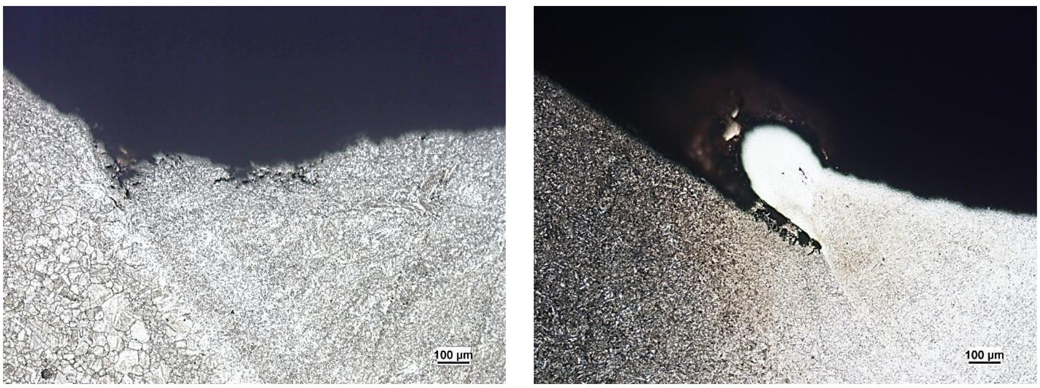

Fig. 7 Corrosion attack in the weld toe locality

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Traces of intercrystalline attack of the welded unfinished AISI 316L were observed only in weld metal and in heat affected zone. Specimens with ground surface did not corrode. The welded unfinished steel AISI CA6-MN for turbine production was susceptible to intercrystalline corrosion only in the weld toes were corrosion was intensive (**Fig. 6**). In the weld toes were identified crevices created by welding and these places are very danger from corrosion point of view. By mechanical finishing they can be removed.

Conclusions

- The short part of the corrosion research of welded stainless steel show that surface treatment after welding is a very important for safe operation and lifetime of products and devices made from this material. Creation undesirable oxide products have not protective effect of passive layer of stainless steel with austenitic or ferritic structure.
- Unfinished surfaces have lower corrosion resistance to pitting and intercrystalline corrosion. Electrochemical stability presented by corrosion potential is lower and corrosion rates of the tested steels are higher.
- The corrosion resistance can be considerably increased by proper surface treatment after welding and heat treatment. On the clean surface (free of product formed after heat affecting) a passive layer with high corrosion protective effect is created. By this way corrosion resistance can be increased.
- Corrosion attack is very danger because it can works as nucleus of crack. The devices and products of stainless steels are mostly hard mechanically loaded ant it can cause their premature failure.

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