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CORROSION BEHAVIOUR OF THE WELDED STEEL 1.4313/CA6-NM

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1.Abstract

The stainless steel 1.4313/CA6-NM (EN X3CrNiMo13-4) is used for turbine production. The weld joints are therefore very sensitive localities from mechanical and corrosion point of view. The subject of the work is corrosion studying of the steel welded by TIG method with consequent heat treatment. Corrosion resistance of the weld joints and base material are evaluated through potentiodynamic polarization test measured on the surface after heat treatment and on the surface cleaned by grinding and polishing. Potentiodynamic polarization tests were carried out in normal mineral water with pH 5 and at room temperature.

2.Introduction

Stainless steels and corrosion resistant alloys may suffer local corrosion, such as pitting and crevice corrosion, mostly in chloride containing oxidizing environments. The behavior of stainless steels with respect pitting or crevice corrosion has been studied extensively by many authors over the last 50 years on the basis of different laboratory approaches [1-6]. Pitting and crevice initiation occur 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).

Their corrosion resistance of these materials after welding may be affected by [7]:

- 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.

Corrosion resistance of the influenced regions can be restored mechanically or chemically and their combination. Grinding or wire brushing might not be sufficient to repair a heat-tinted region [8].

3.Experiments and results

Experimental material

Experimental material is the ferritic stainless steel 1.4313/CA6-NM (DIN X4CrNi134, EN X3CrNiMo13-4, AISI CA6-NM) with chemical composition in Tab. 1

Tab. 1 *Chemical composition of the* steel 1.4313/CA6-NM

Element/wgh. %	**C**	**Mn**	**P**	**S**	**Si**	**Ni**	**Cr**	**Mo**	**N**
min.	-	0.50	-	-	-	3.5	12.4	0.35	0.020
	0.029	0.65	0.019	0.0005	0.32	3.7	12.8	0.56	0.029
max	0.060	1.05	0.035	0.0180	0.65	4.6	14.1	0.75	0.055

The weld joints were made by the TIG methods with filler (EN ISO 17633-A T 13 4 M M 2) in argon protective atmosphere. Chemical composition of the filler metal is in Tab. 2.

Tab. 2 *Chemical composition of the filler metal*

Elements	**C**	**Mn**	**Si**	**P**	**S**	**Cr**	**Ni**	**Mo**
wgh. %	0.018	1.32	0.75	0.014	0.011	12.8	4.52	0.49

After welding the specimens were 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). 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. The base material is ferritic, annealed steel with carbidic network on grain boundaries. In heat affected zone and in weld metal no defects are observed.

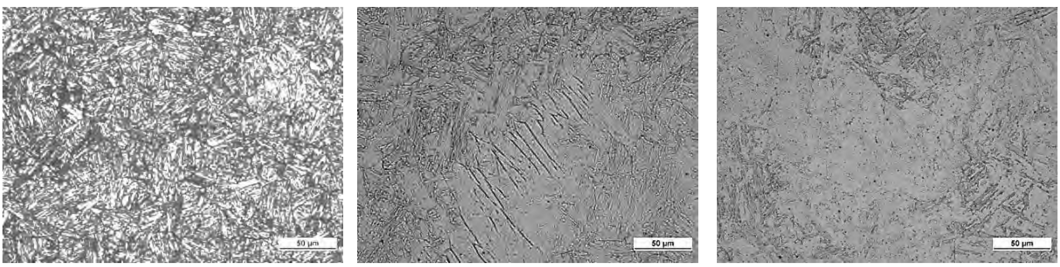

Fig. 1 *Microstructure of the base metal, heat affected zone and weld metal after heat treatment*

For quality evaluation of weld joint microhardness was measured on metallographic scratch pattern in the cross section of weld locality (STN EN ISO 9015-2, measurement conformably to Vickers HV05 by hardness tester Zwick/Roell Indentec ZHμ Vickers). The microhardness was measured along a line in the middle of specimen to be caught BM, HAZ and WM. The number of indentations was 30. Distance between the indentations was 1 mm. Results are shown in Tab. 3 and course of measurement in Fig. 2. It can be seen increasing of microhardness in heat affected zone. Differences of the microhardness values in base material and weld metal are negligible.

Tab. 3 *Microhardness HV05 of the welded steel* 1.4313/CA6-NM

mm	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
HV05	292	292	289	282	273	302	361	368	371	380	322	332	332	348
mm	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**
HV05	335	328	346	378	393	378	376	318	298	303	289	306	290	299

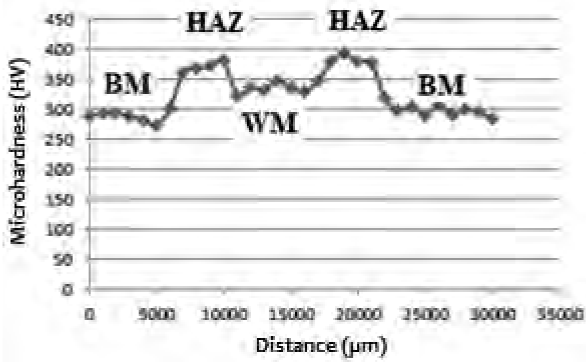

Fig. 2 *The course of microhardness*

Potentiodynamic polarization test

The solution for measurements was prepared of natural mineralized water with pH value 6.8. The pH of the natural water was modified to value pH 5 by addition of HCl, (increasing of chlorides was negligible cca 0.036g Cl in one dm^3 of water) because drop of pH enhances corrosion aggressiveness of water.

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). The tests were performed in locality of base material (both sides) and weld metal (Fig. 3). 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. Eoc, setting delay was 10 minutes and the scan rate was 1 mV/s. 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 Tab. 4 and shown Fig. 4.

Fig. 3 *Localities of potentiodynamic measurement.*

Tab. 4 Results of potentiodynamic tests measured on oxidize surfaces

	E_{corr} [mV]	i_{corr} [μA.cm^{-2}]	b_c [mV]	b_a [mV]	v_{corr} [mm.year^{-1}]
BM	-343.141	5.561	426.6	230.1	0.258
BM	-351.312	3.786	314.2	206.2	0.176
WM	-384.197	1.588	313.6	188.7	0.073

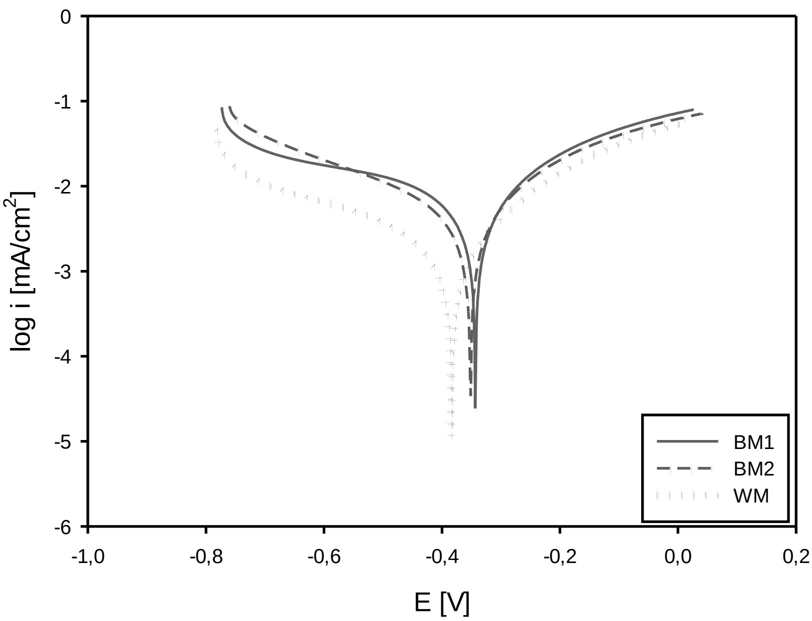

Fig. 4 *Course of potentiodynamic curves of BM and WM on oxidize surfaces*

Because the surface of the evaluated specimens was covered by inhomogeneous gray-black oxides created after welding and heat treatment, result have not expressed real corrosion properties. At normal temperature in air on the surface of stainless steel the Cr_2O_3 is created. The chromium oxide has excellent protective properties and expressively improves corrosion resistivity of stainless steel. For this reason the same type of measurement was made on clear surface of BM and WM. In Tab. 5 it can be seen the differences of corrosion behavior of the evaluated stainless steel and weld metal. Comparison of the corrosion characteristics measured on the evidently oxidize surface and clean surface are different, what confirmed strong influence of surface treatment after heat affecting of stainless steels. Corrosion potential of clean surfaces is above 150 mV more noble than the oxidize ones. Corrosion rate of BM with clean surface is low order beside oxidize one. Differences of corrosion rates measured in weld metal are less too (fig. 5).

Tab. 5 *Results of potentiodynamic tests on non-oxidize surfaces*

	E_{corr} [mV]	i_{corr} [mA.cm^{-2}]	b_c [mV]	b_a [mV]	v_{corr} [mm.year^{-1}]
BM	-217.231	0.797	293.1	321.5	0.037
WM	-230.417	0.889	277.2	258.0	0.041

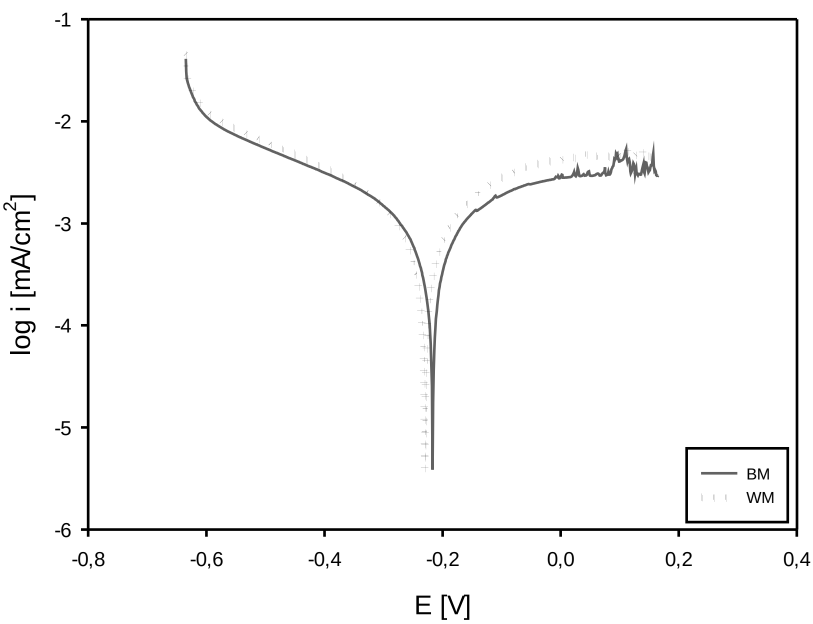

Fig. 5 *Course of potentiodynamic curves of BM and WM on non-oxidize surfaces*

The welded steel for turbine production has not reduced susceptibility to corrosion in comparison to base material. The problem could originate in weld toes if the weld joint is not properly wrought because of service origination. Crervices are from corrosion point of view very danger for this type of steel. In Fig. 6 it can be seen corrosion attack of the steel 1.4313/CA6-NM after test to intergranular corrosion (STN EN ISO 3651-2.) in the weld toe. In base material and weld metal no corrosion attack was contemplated but in weld toes corrosion attack was very intensive.

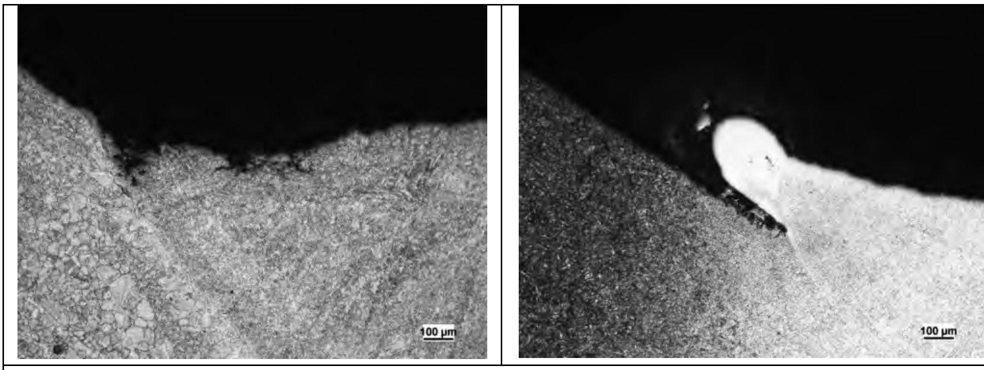

Fig. 6 *Corrosion attack in the weld toe locality*

4. Conclusions

- The weld joints in the stainless steel 1.4313/CA6-NM are without defects. The turbine steel is demanded to have high mechanical properties and corrosion resistance too because of severe operating conditions. According to metalographic evaluation, microhardness measurement and potentiodynamic tests it is possible to suppose that welding did not affected these properties.
- Corrosion resistance studied in natural water with reduced pH to 5 is good. No local attack was observed. The sensitive localities are weld toes if the surface is not treated after welding.
- Only risk of decreased corrosion resistance is in the weld toe, when the crevice created in this area is not treated properly.
- 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.

5. Acknowledgement

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