Investigation of intergranular corrosion welded joint of austenitic stainless steel by electrochemical methods

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Abstract. Sensitization degree of the austenitic stainless steel welded joints was investigated by electrochemical methods: the double loop electrochemical potentiokinetic reactivation (DL EPR) in H_2SO_4 + KSCN solution and by of the corrosion potentials measurement of the steel in the solution drop of HNO_3 + $FeCl_3$ $6H_2O$ + HCl. The welded joints, by an X-ray radiographic method on possible presence of the weld defects, were tested. Grain size of the base metal and the welded joints, by applying an optical microscopy were determined. The existence of compatibility between the results for different electrochemical methods is shown. Heat affected zone (HAZ) of the austenitic stainless steel welded joints has shown significant degree of sensitization. The corrosion potentials measurement method is simple, nondestructive method, that gives qualitative informations about degree of the sensitizations of the stainless steel. The double loop electrochemical potentiokinetic method gives quantitative evidence about susceptibility of the stainless steel to intergranular corrosion. This method can be applied with some adaptation in field environments.

Keywords: stainless steels, welded joints, intergranular corrosion, test methods, electrochemistry.

1. Introduction

Intergranular corrosion is a form of local corrosion, which is manifested by dissolving the grain boundary area. At slow cooling or heating of austenitic stainless steel in the temperature range between 420 to 820°C, at the grain boundaries, chromium carbides precipitates, which causes its depletion near grain boundary area, and steel becomes senzibilitized to intergranular corrosion [1-4]. In order to prevent the occurrence to intergranular corrosion, it is necessary to carry out one of the following procedures: thermal treating of welded structures in order to equalization chromium concentration, applying steel with very low carbon content (<0.04% C) or applying stabilized steel, i.e. steel alloyed with Ti or Nb [5]. Often, it is necessary to increase the contents of Ni and Cr in the additional material, in order to compensate losses of these metals during welding [3].

Traditionally, testing of sensitization degree is performed by chemical treatment of samples in boiling solution of different acids such as H_2SO_4 + $CuSO_4$ in Strauss's method, H_2SO_4 + $Fe_2(SO_4)_3$ in Streicher's and HNO_3 in the Huey test. These examinations take a long time to perform, depending on the type of test, and they may last up to 10 days [6]. The testing methods, using double loop electrochemical potentiocinetic reactivation (DL EPR, method Chigal) are performed in much less time, and quantitative results are obtained. The potential first shifts from corrosion potential to the area of passivation, and then turn to the corrosion potential. In first part of the loop, the dissolution of grains and grain boundaries occur, whereas in the backward part of the loop only the dissolution of grain boundaries occur. Ratio between current peak of reactivation loop and current peak of passivation loop is a measure of the steel tendency towards intergranular corrosion [7-10]. Tomashov and et al. have developed a qualitative method for determination of sensitization degree by measuring the corrosion potential of steel in a drop of the appropriate solution. Steel is considered to be resistant to intergranular corrosion if a positive value of corrosion potential is obtained, and non resistant if a negative value is given in relation to saturated calomel electrode (SCE). This is a simple, qualitative, nondestructive technique for corrosion testing that does not require expensive equipment [11-13].

2. Experimental part

2.1. Material and welding conditions

In table 1 the chemical composition of stainless steel 19Cr-9Ni (AISI 304) which is determined by spectrophotochemical method is given. TIG welding process was carried out in a protective argon atmosphere and for additional material it is used electrode wire G 19 9 L Si (EN 12072).

Table 1. Chemical composition of the stainless steel 19Cr-9Ni.

Element	Cr	Ni	C	Mn	Si	S	Fe
wt. %	18.90	9.22	0,07	1,64	0,50	0,006	Rest.

Arc welding plate was carried out on prepared slot with X shape. Welding was performed with standard TIG process in 6 passes. The quality of welded joint, or possible presence of cracks, pores or similar defects in the welded joint were checked by radiographic method, using X-rays on industrial rendgen Baltpost 200 kV, 135 kV in voltage and current of 5 mA. Radiographic image of a sample stainless steel 19Cr-9Ni with welded joint, where line defect was observed, caused by welding, is shown in Figure 1 (arrow in the picture shows the place of error in the welded joint). This sample was selected and not further investigated to intergranular corrosion. On the other samples, defects or errors in the welded joints were not noticed.

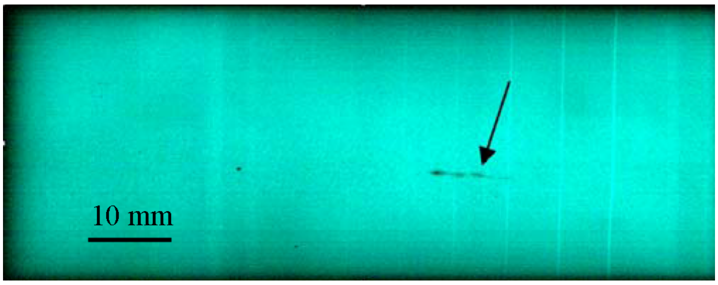

Figure 1. Radiographic picture of the welded joint with linear defect.

Before performing test for determination sensitization degree of stainless steel samples were prepared in the usual procedure. All mentioned potentials are given compared to saturated calomel electrode (SCE).

2.2. Electrochemical potentiocinetic reactivation

Susceptibility to intergranular corrosion is determined using an electrochemical potentiocinetic reactivation method with double loop (DL EPR) in a solution of 0,5 mol dm^{-3} H_2SO_4 + 0,01 mol dm^{-3} KSCN [7]. The tests were carried out close to the weld metal in the heat-affected zone, weld metal and base metal. Saturated calomel electrode (SCE) is used as reference electrode and platinum mesh as counter electrode. To perform the test GAMRY, References 600, potentiostat / galvanostat / ZRA was used. Potential sweep rate was 2 mV / s, starting from the corrosion potential (between -350 mV and -450 mV) where the sample was held for 5 minutes, and then the potential was shifted to the passive state (300 mV) with the same potential sweep rate (passivation loop). Immediately after reaching this potential, the direction of polarization was changed and the sample was returned (reactivation loop) to the corrosion potential. Current ratio of the reactivation peak to the passivation peak (*I*r / *I*p) taking into account the grain size (G) is a measure for the sensitization degree of stainless steel to intergranular corrosion.

2.3. Corrosion potential measuring

Method consists in measuring the corrosion potential of steel in the drop of the solution of 5 % HNO_3 + 20 g dm^{-3} $FeCl_3$ $6H_2O$ + 90 g dm^{-3} HCl, room temperature, on the surface of stainless steel (base metal, HAZ and weld metal) [9,11,12]. Corrosion potential of stainless steel was measured in a time of 120 s. Base metal, HAZ and weld metal in 5 places were controled. Stainless steel is considered to be resistant to intergranular corrosion if is a positive value of corrosion potential obtained ($E_{corr} > 0$) and prone, if it is obtained a negative value of the corrosion potential ($E_{corr} < 0$).

2.4. Metallographic testings

In order to observe easily the position of welded joint metal, the samples were treated in a solution of composition: 20 cm^3 destilovane vode + 4 g $CuSO_4$ $5H_2O$ + 20 cm^3 HCl (ρ = 1,19 g cm^{-3}) [14]. Etching was performed at room temperature in the range of 1-3 min. To detrmine a grain size (G), which is used in calculating the sensitization degree, an optical microscope Neophot 30, with digital camera Sanyo color CCD, was used, in accordance with ISO 643 [15]. Grain size was determined at magnification of 100x in heat-affected zone, as well as in base metal. The microstructure of weld metal, heat-affected zone and base metal, was determinated by magnification of 250x.

3. Results and discussion

3.1. Results of metallographic testing

On Figure 2 are shown the welded stainless steel 19Cr-9Ni macrostructure, microstructure of base metal (2a), heat-affected zone (2b), fusion line (2c) and weld metal (2d). Grain size is determined according to ISO standard [15]. The grain size in base metal was G8, and in HAZ approximately G6-G7, because grain size in heat affected zone could not be precisely determined. Grain size in weld metal could not be determined, due to dendritic structure of weld metal (Fig. 2d).

3.2. Electrochemical potentiocinetic reactivation

The testing results of sensitization degree in stainless steel are shown in Figures 3-5, for the measuring places in base metal (Figure 3), heat-affected zone (Figure 4) and in weld metal (Figure 5). The experimental curves of passivation (→), with appropriate passivation current peak (I_p) and the reactivation curve of the sample (←), with a corresponding reactivation current peak (I_r) are shown.

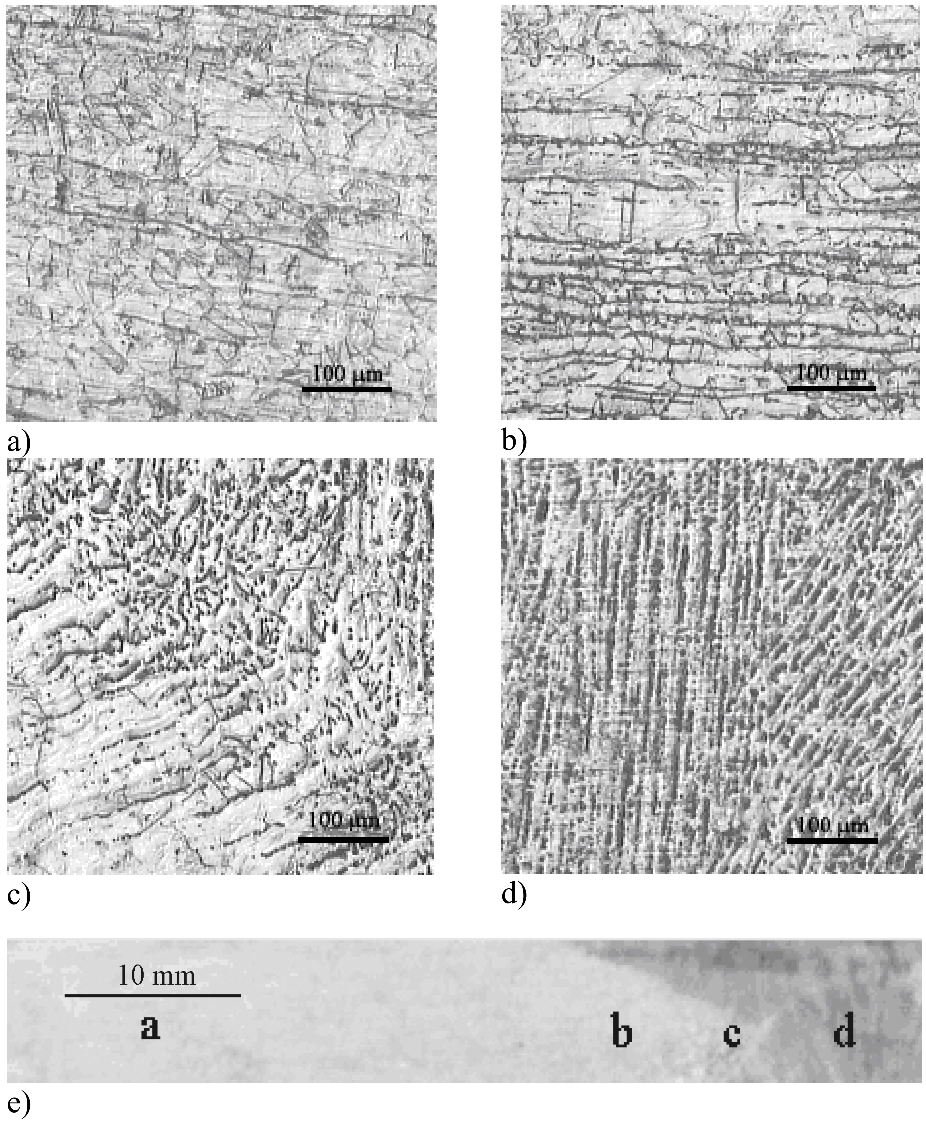

Figure 2. Microstructure of the welded joint: a) base metal, b) heat affected zone, c) fusion line, d) weld metal and e) macrostructure of the welded joint with places of shooting.

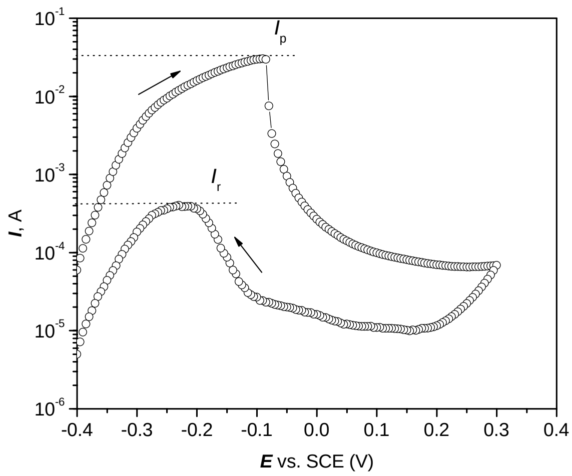

Figure 3. DL EPR testing of the base metal.

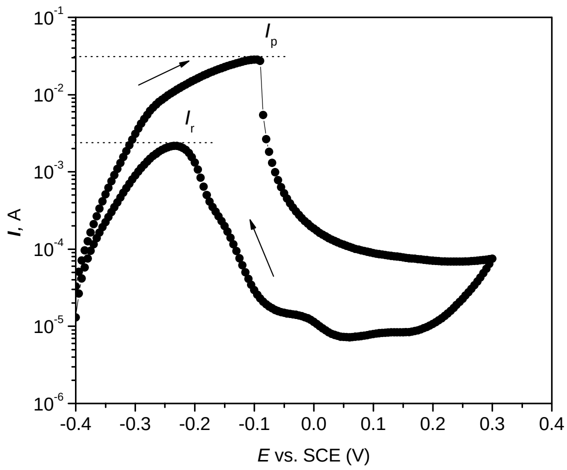

Figure 4. DL EPR testing of the heat affected zone.

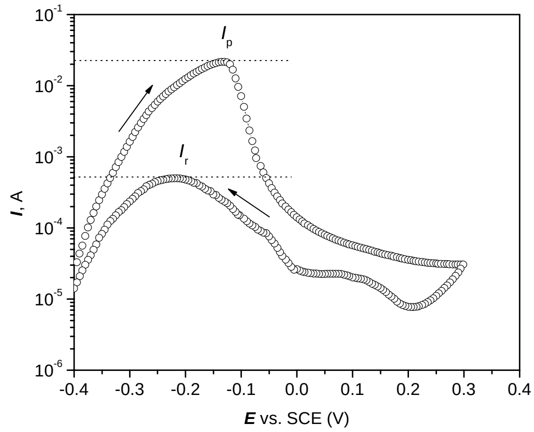

Figure 5. DL EPR testing of the weld metal.

In Table 2 are given the values of passivation current peak (I_p), reactivation current peak (I_r), and their ratio (I_r/I_p). Calculation of the sensitization degree $(I_r/I_p)_{GBA}$, which in by I_r, I_p, is also dependent on grain size, G, is derived using the equation given in the ISO standard [7].

Table 2. DL EPR testing results of the stainless steel 19Cr-9Ni.

Measurement place	E_{kor} (V vs. SCE)	I_p (A)	I_r (A)	I_r/I_p	Grain size	$(I_r/I_p)_{GBA}$
Base metal	-0,430	0,0320	0,00042	0,0131	G8	1,45
HAZ	-0,420	0,0310	0,00220	0,0710	G6-G7	11,1-15,7
Weld metal	-0,435	0,0240	0,00050	0,0208	-	-

Stainless steel is prone to intergranular corrosion, according to ISO standard [7], if the $I_r/I_p > 0.05$, or $(I_r/I_p)_{GBA} > 20$. Steel is resistant to intergranular corrosion if $I_r/I_p < 0.01$. Between those limits, stainless steel is slightly prone. The results (Figures 3-5) show that the base metal is almost resistant to intergranular corrosion. I_r/I_p value, slightly larger than 0.01 (0.0131), is probably due to the existence of a number of active pits on the surface on stainless steel, either within grains or grain boundaries. Heat-affected zone is prone to intergranular corrosion, according to ISO standard [7]. However, according to the GOST standard [9] steel can be still resistant to intergranular corrosion. Therefore, it can be considered that the steel is on the limit-line of susceptibility for this type of corrosion. Weld metal has I_r/I_p value within slightly sensitization to corrosion. Since the weld metal, due to the existence of structural and chemical heterogeneity (Fig. 2d), is susceptible to pitting corrosion than to the base metal [1,5], it has a little higher ratio of I_r/I_p.

3.3. Measurements of corrosion potential

In Table 3 are given the results of measurements of corrosion potential of stainless steel 19Cr-9Ni in a drop of solution. Four of the five measurements on base metal and weld metal gave a positive value of corrosion potential. In such cases, it can be considered that the base metal and weld metal are resistant to intergranular corrosion [9].

Table 3. Corrosion potential measurement results of the stainless steel 19Cr-9Ni.

No.	$E_{corr.base.metal}$ (mV)	$E_{corr.HAZ}$ (mV)	$E_{corr.weld.metal}$ (mV)
1	425	-315	450
2	495	-280	485
3	440	-295	-280
4	-275	-320	475
5	435	-335	445

Based on the results, shown in Table 3, it can be concluded that the weld metal and base metal are resistant to intergranular corrosion resistant, while the heat-affected zone is prone to this type of corrosion.

4. Conclusions

Sensitization degree of the austenitic stainless steel 19Cr-9Ni of welded joints was investigated by electrochemical methods: the double loop electrochemical potentiokinetic reactivation (DL EPR) in H_2SO_4 + KSCN solution and by the corrosion potentials measurement of the steel in the solution drop of HNO_3 + $FeCl_3$ $6H_2O$ + HCl. The quality of the welded joint is controlled by radiographic method, using X-rays, and grain size was determined using an optical microscope.

The method for measuring corrosion potential, in order to determinate the susceptibility to intergranular corrosion, is a simple, qualitative, non-destructive method, that requires no expensive equipment. This method showed that the base metal and weld metal are resistant to intergranular corrosion, while the heat-affected zone (HAZ) is prone.

Electrochemical potentiocinetic reactivation method with a double loop (DL EPR) is a quantitative method for testing the sensitization degree of stainless steel. By using this method it is possible to see small differences in the susceptibility to intergranular corrosion, especially if the sensitization degree is not high. Test results, using the DL EPR method, showed that the base metal and weld metal are slightly prone to intergranular corrosion, while the heat-affected zone (HAZ) is on the limit-line of high susceptibility to this type of corrosion. There is a considerable degree of agreement for test results, according to the sensitization degree to intergranular corrosion of stainless steel 19Cr-9Ni obtained by DL EPR method, with the results by measuring the corrosion potential in drop of the solution.

Senzibilizated structure of stainless steel is susceptible to stress corrosion cracking, in the presence of stress, outside or intside stress (caused during the welding), and adequate corrosion envirement (Cl^- ions). It means, that these tests show a susceptibility of stainless steel to stress corrosion cracking and pitting corrosion, also.

Acknowlegements:

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