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# Investigation of possibility for reducing AISI 303 stainless steel pitting corrosion by microalloying with boron or zirconium

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**Abstract:** AISI 303 has the highest machinability comparing with all other austenitic stainless steel grades. The good machinability is result of sulphur presence in the steel composition. Sulphur improves machinability but at the same time causes a decrease in the corrosion resistance. The aim of the research was to examine the possibility of reducing the effect of sulfur content on the corrosion behavior of AISI 303 by microalloying with boron or zirconium. The intention is to keep high machinability of this steel grade but make it corrosion resistant. The results show that after microalloying with boron or zirconium the intensity of pitting corrosion of AISI 303 stainless steel can be significantly reduced. The results show that the effect of reducing the intensity of pitting corrosion of AISI 303 stainless steel microalloyed with boron or zirconium is higher at lower concentrations of chlorides. This is confirmed trough comparing the intensity of pitting corrosion of the 303 stainless steel samples microalloyed with boron or zirconium with the samples of 304 stainless steel. The intensity of pitting corrosion 303 stainless steel microalloyed with boron or zirconium is closer to the intensity of pitting corrosion of 304 stainless steel in 1.5% NaCl solution than in a 3% NaCl solution. Results also clearly indicate that the increase of NaCl concentration leads to an increase of pitting corrosion in all tested samples.

## INTRODUCTION

Austenitic stainless steels are among the most widely used types of stainless steel. The most commonly used grades are 300 series of alloys according the American Iron and Steel Institute (AISI). Starting from the basic 304 alloy (Fe-19Cr-10Ni), Mo is added to improve resistance to pitting (2-3 wt.% in the case of type 316 and 3-4 wt.% in type 317). Sensitization due to Cr depletion during welding and other heat treatments, and the possible resultant intergranular corrosion, can be avoided through the use of low-carbon grades (304L, 316L, 317L, in which C is limited to 0.03 wt.% max.) or by adding Ti (type 321) or Nb and Ta (type 347) to precipitate C at higher temperatures. The addition of Cr also imparts greater oxidation resistance, whilst Ni improves the ductility and workability of the material at room temperature (F. King, 2009). Stainless steel has important characteristics such as versatility, durability, attractiveness and high mechanical and corrosion resistance (Kikuti et al. 2004).

Grade 303 is the most readily machinable of all austenitic grades of stainless steel. The good machinability of grade 303 is due to the presence of sulphur in the steel composition. Whilst the sulphur improves machining, it also causes a decrease in the corrosion resistance and a slight lowering of the toughness. The effect of sulfur on the corrosion behavior of austenitic stainless steel is manifested through the behavior of the sulfide inclusions due to the low solubility of sulfur in ferrous metals. sites for localized corrosion for almost 100 years, for steels, and for almost 60 years for stainless steels. The effect of an alloying element can be manifested through effects on the passive film, the local solution chemistry, or the interfacial electrochemical kinetics (Donik et al. 2010). The corrosion resistance of type 303 is lower than that for 304 stainless steel. Type 303 is usually compared with type 304 stainless steel because they have nearly the same chemical composition except for the addition of sulfur in type 303. The toughness is still excellent comparing with other austenitic grades. Grade 303 is used in applications that require parts to be heavily machined. These applications include nuts and bolts, screws, gears, aircraft fittings, bushings, shafts, etc. Sulphur additions to the composition act as initiation sites for pitting corrosion. However, corrosion resistance remains good in mild environments. In chloride containing environments over 60°C, 303 stainless steel is subjected to pitting and crevice corrosion. Grade 303 stainless steel is not suitable for use in marine environments (Atlas Specialty Metals, 2003). Stainless steels generally are subjected to pitting corrosion. Pitting corrosion represents an important limitation to the safe and reliable use of many alloys in various industries. Pitting is characterized by more or less local points of attack with considerable depth and normally occurs on free surfaces. Pitting is a very serious type of corrosion damage because of the rapidity of metallic sections perforation. Pitting corrosion is defined as an extremely localized corrosive attack (Bikić, 2013). Simply stated, pitting is the type of localized corrosion that produces pits, that is, sites of corrosive attack that are relatively small compared to the overall exposed surface (Shreir, 1994).

Pitting corrosion of stainless steels is manifested by the rapid growth of current flow after achieving specific values of anode potential after pits formation. Pitting corrosion can be prevented if the anions present in solution hinder the adsorption of chlorides, or push them from the metal surface. Adding other anions in the solution containing chlorides (chromate, nitrate, Sulfide inclusions have been recognized as preferential environmentally-friendly organic compounds…) moves the value of pitting potential in anodic area.

The resistance to pitting corrosion can be enhanced by increasing the content of chromium, molybdenum and nitrogen in the stainless steel composition. In order to reduce the intensity of pitting corrosion stainless steels are mainly alloyed with molybdenum (ASM International, 1992). For research described in this paper in order to reduce the intensity of pitting corrosion 303 stainless steel is microalloyed with boron or zirconium. Boron in stainless steels increases resistance to general corrosion in acidic environments (Guo Tie-ming et al. 2013). The presence of zirconium in stainless steels also increases corrosion resistance (Cheng Wei-Jen, et al. 2013).

## EXPERIMENTAL

The aim of the research was to examine the possibility of reducing the effect of sulfur addition on pitting corrosion in 303 stainless steel microalloying with boron or zirconium. The intention is to keep good machinability of 303 stainless steel but try to make it corrosion resistant. Production of 303 stainless steel microalloyed with boron and zirconium was performed in a vacuum induction furnace with capacity of 20 kg at the Metallurgical Institute"Kemal Kapetanović" in Zenica.

Samples of 304 stainless steel were prepared using commercial 304 stainless steel. Investigations were conducted in the corrosion cell according to Standard ASTM G5, on instrument potentiostat/galvanostat, Princeton Applied Research, model 263A-2, with the software PowerCORR® (Standard, ASTM G5-94). Method of cyclic polarisation was used for corrosion investigation. Corrosion tests were performed on AISI 303 and AISI 304 stainless steels (chemical compositions are given in Table 1).

Investigation was performed in 1,5 and 3,0% NaCl solutions. Tests were performed at room temperature, 20±1°C.

**Table 1.** Chemical composition of the tested stainless steels

| Number of sample | Chemical composition (wt.%) | | | | | | | | | Type to AISI |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | P | S | Cr | Ni | B | Zr | |
| 1 and 5 | 0,03 | 0,42 | 0,61 | 0,021 | 0,18 | 18,3 | 9,4 | - | - | 303 |
| 2 and 6 | 0,05 | 0,47 | 0,66 | 0,021 | 0,19 | 18,5 | 9,5 | 0,004 | - | 303 |
| 3 and 7 | 0,04 | 0,35 | 0,75 | 0,021 | 0,17 | 18,8 | 9,4 | - | 0,016 | 303 |
| 4 and 8 | ≤0,07 | ≤1,0 | ≤2,0 | max 0,045 | ≤0,015 | 17,5-19,5 | 8,0-10,5 | - | - | 304 |

## RESULTS AND DISCUSSION

To test pitting corrosion, samples of stainless steel the method of cyclic polarization were used. The method of cyclic polarization includes scanning of the potential to a vertex potential and reverses at the current threshold after crossing the vertex potential. Scan rate was 0.5 mV/s. Pitting corrosion of stainless steels is manifested by the rapid growth of current at achieving specific values of anode potential, pitting potential ($E_{pitt}$), Figure 1. Pitting potential is the potential at which pitting starts and that phenomenon is noticed when the current of the polarization curve suddenly starts to rise. According to the present understanding of the pitting corrosion process the Epitt represent critical threshold value, where metastable pits nuclei within the passive state of the stainless steel may be transformed into stable growing pits when the passive formation breaks down (Loto et al. 2013).

Negative values of pitting potential mean that steel is prone to pitting corrosion. Surface of hysteresis loop is generally measure of the intensity of pitting corrosion, Figure 1. Larger surface loop means higher intensity of pitting corrosion (Bikić, 2010). The results of pitting corrosion tests of investigated stainless steels are given in Figures 2 to 7.

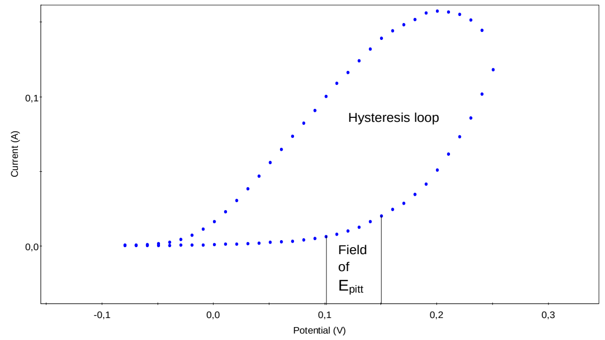


**Figure 1**. Cyclic polarization curve

Samples 1, 2, 3 and 4 (Table 1) were tested in a 3% NaCl solution. Samples 5, 6, 7 and 8 (Table 1) were tested in a 1,5% NaCl solution. Figures 2 and 3 show the effect of the concentration of chlorides, added over NaCl, on intensity of pitting corrosion of tested stainless steels samples.

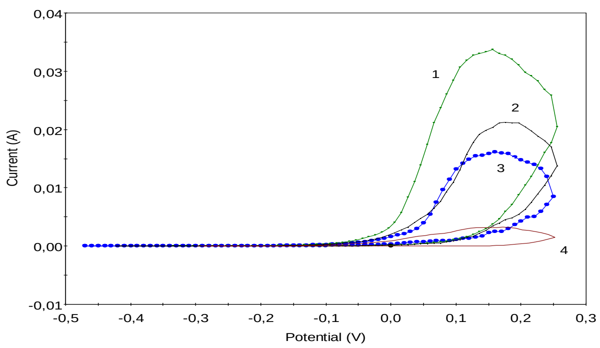


**Figure 2.** Cyclic polarization curves of samples tested in 3% NaCl solution

Figures 2 and 3 show that, after microalloying of 303 stainless steel with boron or zirconium, the intensity of pitting corrosion is reduced significantly. Comparing the cyclic polarization curves of samples 1, 2, and 3 (Figure 2), as well as samples 5, 6 and 7 (Figure 3) decrease in the surfaces of hysteresis loop of the samples 2 and 3 in relation to surface of hysteresis loop of the sample 1 (Figure 2) as well as the samples 6 and 7 in relation to the sample 5 (Figure 3) is evident. Reducing the surface of hysteresis loop of 303 stainless steel samples microalloyed with boron or zirconium compared to 303 stainless steel that is not microalloyed with mentioned elements, is much more pronounced at lower concentrations of chloride (Figure 3) than at higher concentrations of chloride (Figure 2). This is confirmed by the results of comparing the intensity of pitting corrosion samples of 303 stainless steel microalloying with boron or zirconium with samples of 304 stainless steel.

The intensity of pitting corrosion of 303 stainless steel microalloyed with boron or zirconium is closer to the intensity of pitting corrosion of 304 stainless steel in 1.5% NaCl solution than in a 3% NaCl solution. Namely, it is much better matching of surfaces area of hysteresis loop of the samples 6, 7 to the samples 8 (Figure 3) than surfaces area of hysteresis loop of the samples 2, 3 to the samples 4 (Figure 2).

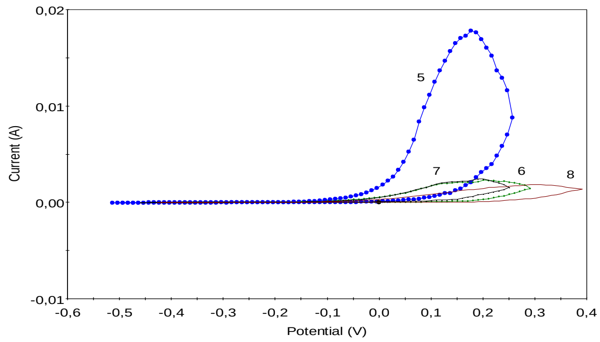


Figure 3. Cyclic polarization curves of samples tested in 1,5% NaCl solution

In general, it can be concluded that 303 stainless steel microalloyed with boron or zirconium becomes much more resistant to pitting corrosion which significantly reduces the effect of sulfur on pitting corrosion. Results also clearly indicate that the increase of NaCl concentration leads to an increase in pitting corrosion in all samples tested. Proof of the above statement is a comparison of pitting potential of samples with same chemical composition treated in solutions with different concentrations of NaCl (Table 2).

Table 2. Values of pitting potential of the tested samples

| Number of sample | Conc. of NaCl solution(wt.%) | Pitting potential, ± 10 mv |
|---|---|---|
| 1 | 3 | 66 |
| 2 | 3 | 76 |
| 3 | 3 | 30 |
| 4 | 3 | 192 |
| 5 | 1,5 | 77 |
| 6 | 1,5 | 86 |
| 7 | 1,5 | 90 |
| 8 | 1,5 | 232 |

Comparing samples 1 and 5, 2 and 6, 3 and 7, 4 and 8, (Table 2), it is evident that increasing of concentrations of NaCl solution leads to reduction of pitting potential. Reducing the pitting potential means less resistance to pitting corrosion. Comparison of surfaces area of hysteresis loops of samples with same chemical composition treated in solutions with different concentrations of NaCl also proves above mentioned conclusion (Figures 4, 5, 6 and 7). Figures 4, 5, 6 and 7 shows that increasing NaCl concentration leads to an increase of surface area of hysteresis loop which also means an increase of intensity of pitting corrosion. Figures 4, 5, 6 and 7 also show an increase of pitting potential with decreasing concentrations of NaCl.

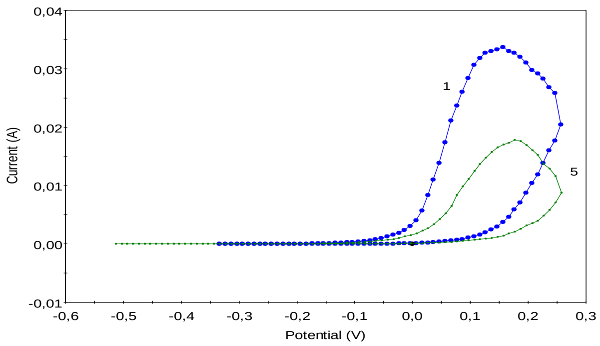

**Figure 4.** Comparison of cyclic polarization curves

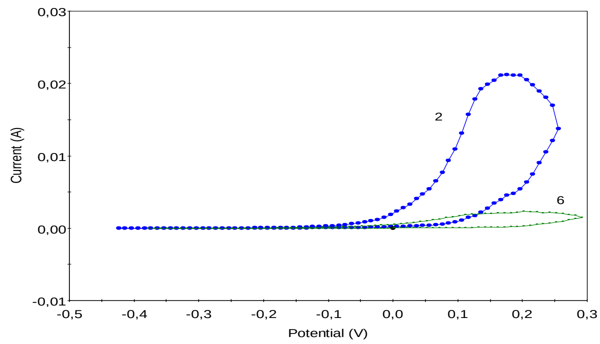

**Figure 5.** Comparison of cyclic polarization curves

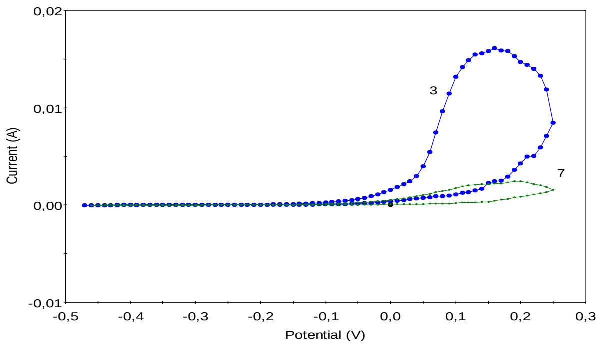

**Figure 6.** Comparison of cyclic polarization curves

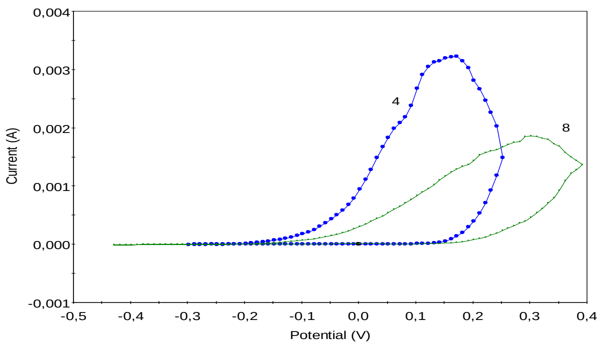

**Figure 7.** Comparison of cyclic polarization curves

## CONCLUSIONS

The results presented in this paper clearly show that the microalloying with boron or zirconium intensity of pitting corrosion of 303 stainless steel can be reduced significantly. This is proven by comparing the intensity of pitting corrosion of 303 stainless steel samples with or without additions of boron or zirconium in solution of 1.5% NaCl and 3% NaCl. The results show that the effect of reducing the intensity of pitting corrosion of 303 stainless steel microalloyed with boron or zirconium is higher at lower concentrations of chloride. This is confirmed trough comparing the intensity of pitting corrosion of 303 stainless steel samples microalloyed with boron or zirconium with 304 stainless steel samples. The intensity of pitting corrosion of 303 stainless steel microalloyed with boron or zirconium is closer to the intensity of pitting corrosion of 304 stainless steel in 1.5% NaCl solution than in a solution of 3% NaCl. Results also clearly indicate that the increase of NaCl concentration leads to an increase of pitting corrosion in all tested samples.

## REFERENCES

King F. (2009). Corrosion Resistance of Austenitic and Duplex Stainless Steels in Environments Related to UK Geological Disposal, A Report to NDA RWM, Quintessa Limited, QRS-1384C-R1,Version 1.2, UK.

Kikuti E., Conrrado R., Bocchi N., Biaggio S.R., Rocha-Filho R.C. ( 2004). Chemical and Electrochemical Coloration of Stainless Steel and Pitting Corrosion Resistance Studies, J. Braz. Chem. Soc., Vol. 15, No. 4, 472-480.

Donik Č., Paulin I., Jenko M. (2010), Influence of MnS inclusions on the corrosion of austenitic stainless steels, Materials and technology 44 (2), 67–72.

Atlas Specialty Metals (2003). Technical Handbook of Stainless Steels, Atlas Specialty Metals Technical Services Department, Australia.

Bikić F., Rizvanović M., Avdušinović H. (2013). Investigation pitting corrosion of ASTM 321 stainless steel, 17th International Research/Expert Conference “Trends in the Development of Machinery and Associated Technology” TMT, Istanbul, Turkey, Proceedings, ISSN 1840-4944, 121-123.

Shreir L.L., Jarman R.A., Burstein G.T. (1994). Corrosion, Metal/Environment Reactions, Butterworth-Heinemann, Great Britain.

ASM International (1992). Handbook Volume 13, Corrosion, ASM International Handbook Committee, USA.

Guo T.M, Hui Z., Nan X.L, Han C.S, Zhang D.C (2013), Influence of the Trace Boron Element on Corrosion Behavior of 1Cr17 Stainless Steel in 10% HCl Solution, Advanced Materials Research Vol. 648, pp 67-72.

Cheng W.J, Sellers R.S., Anderson M., Sridharan K., Wang C.J., Allen T. R. (2013). Zirconium effect on the corrosion behavior of 316 L stainless steel alloy and hastelloy-n superalloy in molten fluoride salt, Nuclear technology vol. 183, 248-259.

ASTM G5 (1994). Standard Reference Test Method for Making Potentiostatic and Potenciodynamic Anodic Polarization Measurements.

Loto R.T. (2013). Pitting corrosion evaluation of austenitic stainless steel type 304 in acid chloride media, J. Mater. Environ. Sci. 4 (4) 448-459.

Bikić F., Ćatić S. (2010). Investigation of uniform and pitting corrosion of 316L stainless steel with and without inhibitor, XXI Congress of chemists and technologists of Macedonia,Ohrid, Book of abstract, 226.

## Summary / Sažetak

Čelik tipa AISI 303 je austenitni nehrđajući čelik koji se najlakše mašinski obrađuje u odnosu na sve druge nehrđajuće čelike zahvaljujući dodatku sumpora. Dodatkom sumpora navedenom čeliku se međutim smanjuje otpornost na koroziju. Cilj provedenih istraživanja je bio ispitati može li se smanjiti efekat dodatka sumpora na povećanje intenziteta piting korozije nehrđajućeg čelika tipa AISI 303, mikrolegiranjem s borom ili cirkonijem. Namjera je zadržati laku obradivost čelika tipa AISI 303 a uz to čelik pokušati učiniti koroziono otpornijim. Rezultati pokazuju da se mikrolegiranjem borom ili cirkonijem intenzitet piting korozije čelika tipa AISI 303 može znatno smanjiti. Rezultati pokazuju da je efekat smanjenja intenziteta piting korozije čelika tipa AISI 303 mikrolegiranjem borom ili cirkonijem veći kod nižih koncentracija hlorida. To potvrđuju i rezultati poređenja intenziteta piting korozije uzoraka čelika tipa AISI 303 mikrolegiranih borom ili cirkonijem s uzorcima čelika tipa AISI 304. Intenzitet piting korozije čelika tipa AISI 303 mikrolegiranog borom ili cirkonijem više se približava intenzitetu piting korozije čelika tipa AISI 304 u otopini 1,5 % NaCl nego u otopini 3 % NaCl. Rezultati takođe nedvojbeno pokazuju da s povećanjem koncentracije NaCl dolazi do povećanja piting korozije na svim testiranim uzorcima.