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Investigation of general corrosion of austenitic stainless steel types 304 L and 317 L, especially from the aspect of their chemical composition

ABSTRACT

Austenitic stainless steels are among the most widely used types of stainless steel. The most commonly used grades are the American Iron and Steel Institute (AISI) 300 series of alloys. Starting from the basic 304 alloy (Fe-19Cr-10Ni), molybdenum is added to improve resistance to pitting (2-3 wt.% in the case of type 316 and 3-4 wt.% in type 317). Sensitisation due to chrome 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 carbon is limited to 0.03 wt.% max.) or by adding titanium (type 321) or niobium and tantalum (type 347) to precipitate carbon at higher temperatures. The addition of chromealso imparts greater oxidation resistance, whilst nickel improves the ductility and workability of the material at room temperature.

In this paper, general corrosion of austenitic stainless steels, specifically low-carbon types 317 L and 304 L, was investigated. The research results are presented in the form of Tafel polarization curves, expressed through corrosion current density and open circuit potential. The results prove that the rate of general corrosion of the tested austenitic stainless steels decreases by lowering the temperature of the HCl solution, decreasing the concentration of HCl, and the presence of molybdenum in the composition of steel type 317 L.

Keywords: *austenitic stainless steels, general corrosion, 317 L, 304 L, Tafel polarization curves*

1. INTRODUCTION

Stainless steels usually excellent resistance to corrosion is down to an ultrathin layer of oxides of especially chromium and iron, and although this film is only a few nanometres thick, it is still so dense and strong that the steel is effectively 'isolated' from the surrounding environment - similarly to an ultrathin paint. If, despite all precautions, a hole occurs in the protective oxide layer, it quickly restores itself, and the steel is again protected. This mechanism is called repassivation [1]. Austenitic stainless steels are among the most widely used types of stainless steel. The most commonly used grades are the American Iron and Steel Institute (AISI) 300 series of alloys. Starting from the basic 304 alloy (Fe-19Cr-10Ni),molybdenum is added to improve resistance to pitting (2-3 wt.% in the case of type 316 and 3-4 wt.% in type 317). Sensitisation due to chrome 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 carbon is limited to 0.03 wt.% max.) or by adding titanium (type 321) or niobium and tantalum (type 347) to precipitate carbon at higher temperatures. The addition of chrome also imparts greater oxidation resistance, whilst nickel improves the ductility and workability of the material at room temperature[2, 3].

In this paper, general corrosion of austenitic stainless steels, specifically low-carbon types 317 L and 304 L, will be investigated. The high corrosion resistance of stainless steel is attributed to the formation of a protective passive film on its surface. Many scholars have studied the characteristics of passive film. By direct imaging of native passive film on 304 stainless steel, Hamada demonstrated the enrichment of chromium in the film and the enrichment of nickel in the matrix side closest to the passive film/matrix interface [4]. Stainless steel

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has important characteristics such as versatility, durability, attractiveness and high mechanical and corrosion resistance [5].General corrosion is also called acid corrosion as it is a type of corrosion that in stainless steel is often found in very acidic, but also in very alkaline media. As opposed to the four other types of stainless steel corrosion, general corrosion is characterised by both anode and cathode reactions taking place all over the surface. This means that the whole surface is activated and thereby corrodes more or less uniformly [1]. In non-passivating metals and alloys, general corrosion is the most common type of corrosion, but for passivatable alloys it is relatively rare. Even in strong acids, stainless steel can achieve a certain level of passivity, and in practice there is a big difference between an acid that simply thins the passive layer, but does not entirely dissolve it, and an acid that eats away the whole of the passive layer and immediately attacks the underlying steel. Relatively weak and pure acids (e.g. citric acid, acetic acid or formic acid) only thin the naturally occurring oxide layer slightly. The oxide layer is restored with the same speed, and corrosion loss is minimal - at least when the acids are pure. If the acids contain aggressive ions (especially chloride), the situation may become far worse, especially at high temperatures [1].

2. EXPERIMENTAL PART

AISI/ASTM 304 L and 317L steels were used for general corrosion testing of austenitic stainless steels. The chemical compositions of the mentioned steels are given in table 1.

Table 1. Chemical composition of tested austenitic stainless steels

AISI/ ASTM	Mas. %								
	C	Si	Mn	P_{max}	S	N	Cr	Mo	Ni
317L	≤ 0,03	≤ 1,00	≤ 2,00	0,045	≤0,015	≤ 0,11	17,5-19,5	3-4	13-16
304L	≤ 0,03	≤ 1,00	≤ 2,00	0,045	≤0,015	≤ 0,11	18 -20	-	10-12

The test of general corrosion of austenitic stainless steels was carried at temperatures of 20 ±1 °C, 30 ±1 °C and 40 ±1 °C, in 0.5% HCl and 1% HCl solutions. The Taffel extrapolation method was used to examine general corrosion of 317 L and 304 L austenitic stainless steels. The Taffel extrapolation method involves scanning the potential of the working electrode of ±250 mV in relation to its open circuit potential $E_{(I=0)}$, at a speed of 0.5 mVs^{-1}. Investigation of corrosion was conducted in a corrosion cell according to the Standard ASTM G5-94 [6], on a potentiostat/galvanostat instrument Princeton Applied Research, model 263A-2, with PowerCORR® software, which is part of the Power Suite softwere package.

3. RESULTS AND DISCUSSION

The results of testing the general corrosion rate of selected austenitic stainless steels, using the Taffel extrapolation method, are shown in tables 2 and 3, but also in figures 1-8.

Table 2 but alsoFigures 1 and 2 show the influence of the concentration of HCl solution on the rate of general corrosion of austenitic stainless steel types 304 L 317 L.

Table 2. Corrosion rate of tested austeniticstainless steels in 0.5% and 1% HCl

AISI/ ASTM	t = 30 ±1 °C, 0,5 % HCl		t = 30 ±1 °C, 1 % HCl	
	$E_{(I=0)}$, mV	i_{cor}, μAcm^{-2} (mmpy)	$E_{(I=0)}$, mV	i_{cor}, $\mu A\ cm^{-2}$(mmpy)
304L	10,823	$7,79(9,06\cdot10^{-2})$	-334,42	$6,71\cdot10^{1}(7,79\cdot10^{-1})$
317L	-22,314	$5,907(6,86\cdot10^{-2})$	-312,90	$3,854\cdot10^{1}(4,48\cdot10^{-1})$

With an increase in the concentration of the HCl solution, there is an increase in the rate of general corrosion for both types of stainless steels, 304 L and 317 L. With an increase in the concentration of the HCl solution, there is an increase in the value of the corrosion current density $i_{cor}$for both types of stainless steels, Table 2 but also Figures 1 and 2. With an increase in the concentration of the HCl solution, the open circuit potential $E_{(I=0)}$ shifts to more negative values for both types of stainless steels, Table 2 but also Figures 1 and 2.

One of the most aggressive ions that cause general corrosion of stainless steels are chloride ions. Chlorides are able to remove the oxide of steel and then attack the steel itself. By adding chloride to an otherwise relatively harmless acid, you get diluted hydrochloric acid which will be far more corrosive to the steel than the pure, chloride-free acid [1].

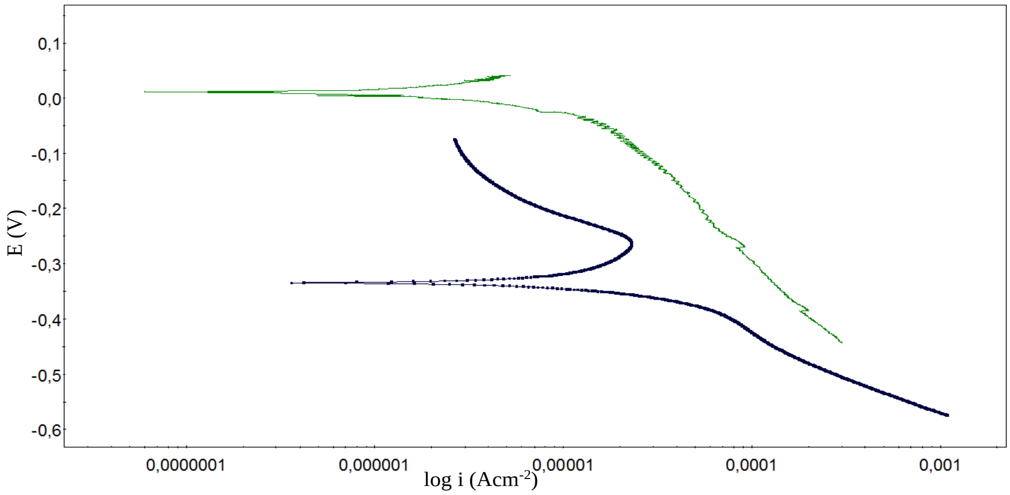

Figure 1. Tafel curves of samples ASTM 304 L (t =30 °C, ---- 1% HCl, ---- 0,5% HCl)

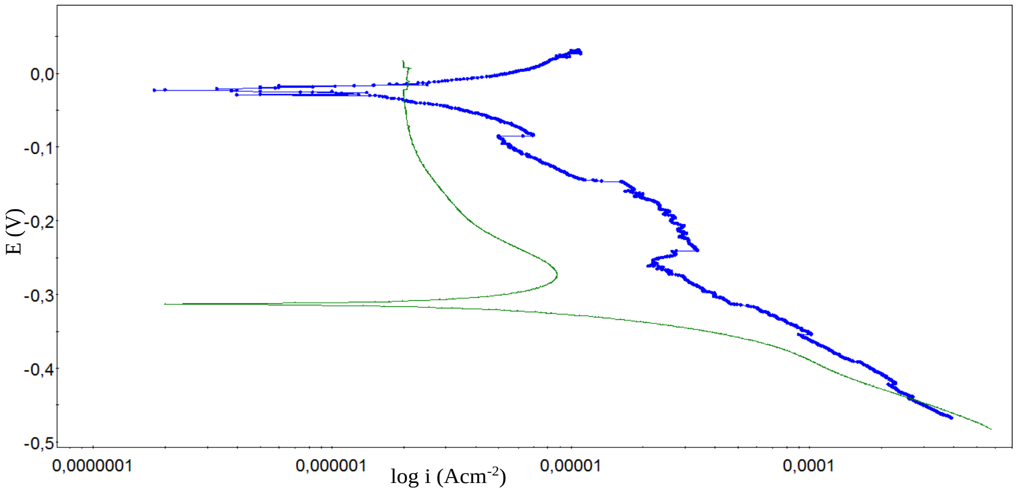

Figure 2. Tafel curves of samples ASTM 317 L (t =30 °C, ---- 1% HCl, ----0,5% HCl)

Table 3 but also Figures 3 and 4 show the influence of temperature on the rate of general corrosion of austenitic stainless steel types 304 L and 317 L.

Table 3. Corrosion rate of tested austeniticstainless steels in 0.5% HCl solution

AISI/ ASTM	t = 20 ±1 °C		t = 30 ±1 °C		t = 40 ±1°C	
	$E_{(I=0)}$, mV	i_{cor}, µAcm^{-2} (mmpy)	$E_{(I=0)}$, mV	i_{cor}, µAcm^{-2} (mmpy)	$E_{(I=0)}$, mV	i_{cor}, µAcm^{-2} (mmpy)
304L	61,07	2,33(2,71·10^{-2})	10,823	7,79(9,06·10^{-2})	-146,71	35,4(4,11·10^{-1})
317L	72,05	5,57(6,47·10^{-2})	-22,314	5,91 (6,86·10^{-2})	-55,413	9,24 (1,07·10^{-1})

With increasing temperature of the HCl solutionthere is an increase in the rate of general corrosion for both types of stainless steels 304 L and 317 L.With increasing temperature of the HCl solution, there is an increase in the value of the corrosion current density $i_{cor}$for both types of stainless steels, Table 3but also Figures 3 and 4. With increasing temperature of the HCl solution, the open circuit potential $E_{(I=0)}$ shifts to more negative values for both types of stainless steels, Table 3 but also Figures 3 and 4. Temperature has an important effect on the corrosion of stainless steels. A rise in temperature will generally lead to a decrease in the corrosion resistance [7].Escrivà suggested that the passive films formed at high temperatures should be more defective[8]. This was beneficial for the mitigation of aggressive ions inside the passive film and consequently could accelerate the dissolution process and the exchange kinetics between the electrode surface and the electrolyte [9]. BenSalah found that higher temperatures tended to promote the for mation of a porous film, thus leading to a decrease in the corrosion resistance[10].

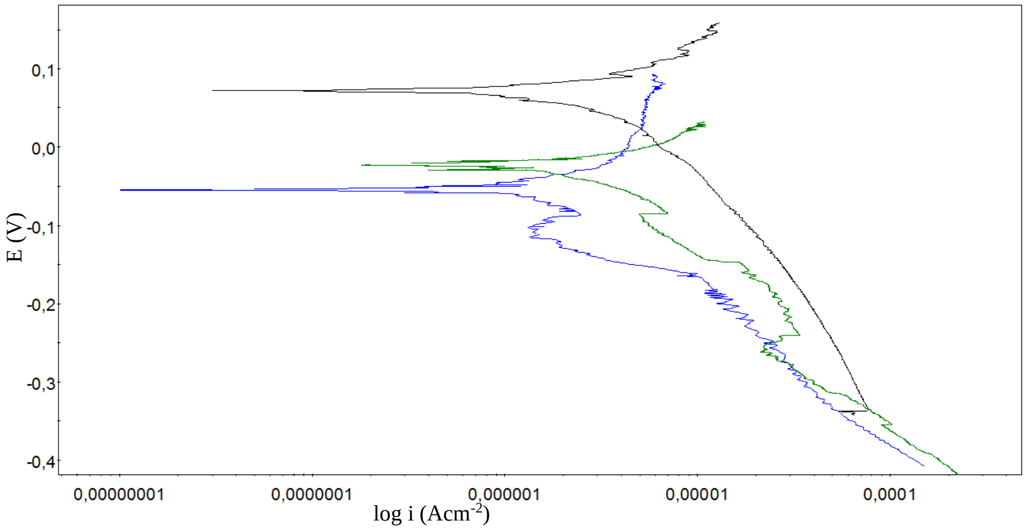

Figure 3. Tafel curves of samples ASTM 317 L tested in 0.5% HCl(---- 40°C, ---- 30 °C, ---- 20 °C)

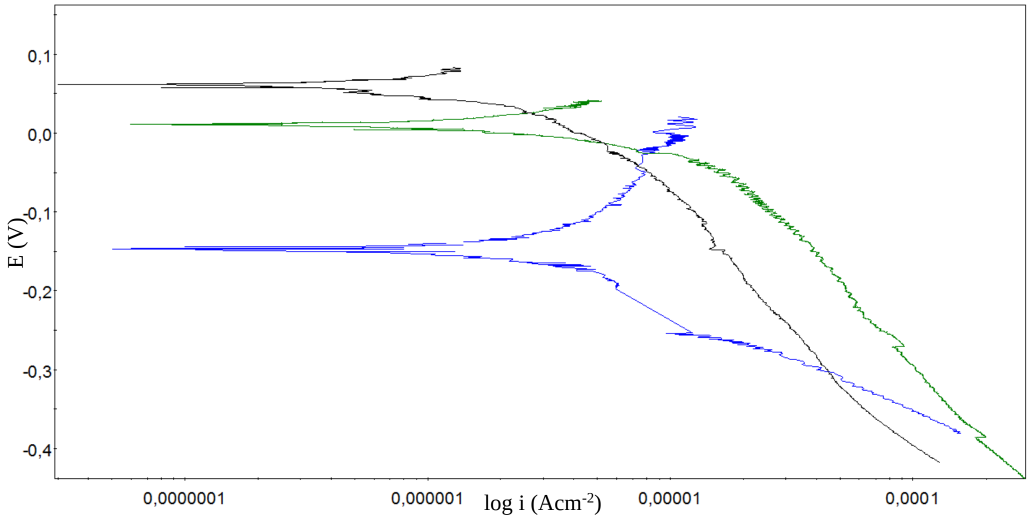

Figure 4. Tafel curves of samples ASTM 304 L tested in 0.5% HCl solution (---- 40°C, ----30 °C, ---- 20 °C)

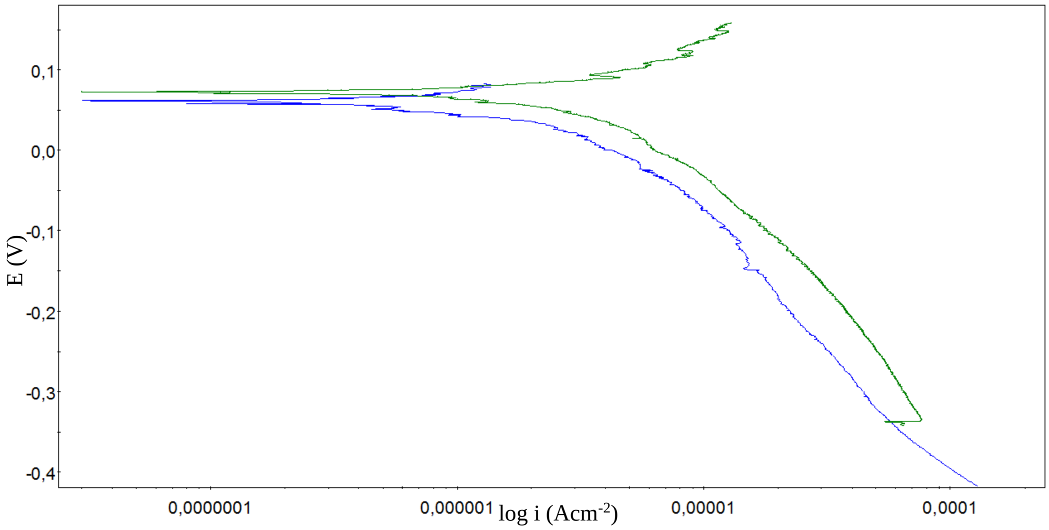

Figure 5. Tafel curves of samples tested in 0.5% HCl solution at 20 °C (---- 304 L, ----317 L)

Tables 2 and 3 but also Figures 5, 6, 7 and 8show the influence of chemical composition on the rate of general corrosion of austenitic stainless steel types 304 L and 317 L.

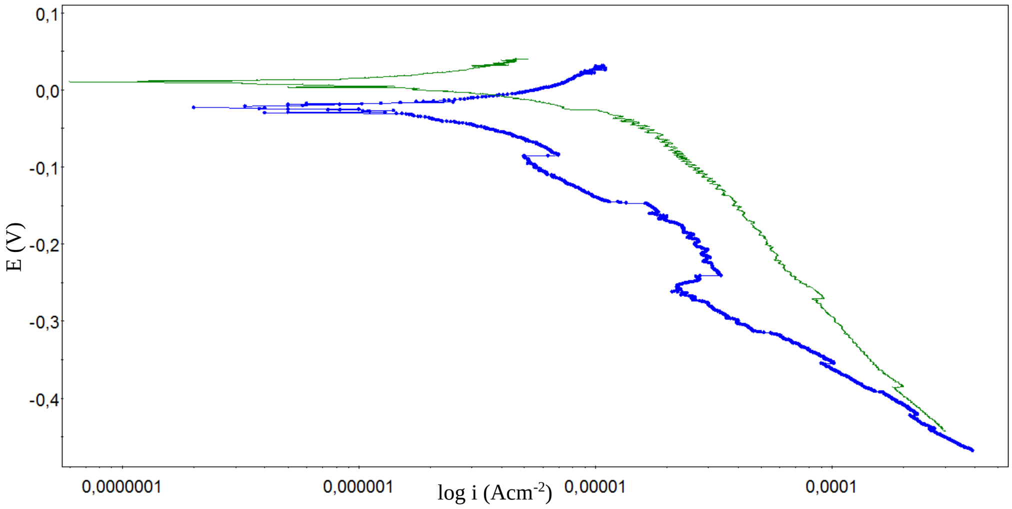

Figure 6. Tafel curves of samples tested in 0.5% HCl solution at 30 °C (---- 317 L, ---- 304 L)

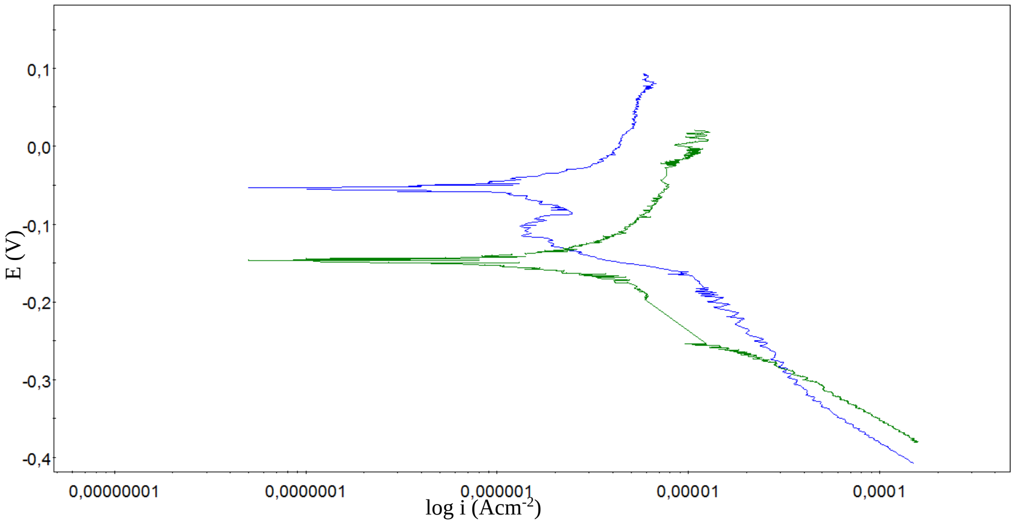

Figure 7. Tafel curves of samples tested in 0.5% HCl solution at 40 °C (---- 317 L, ---- 304 L)

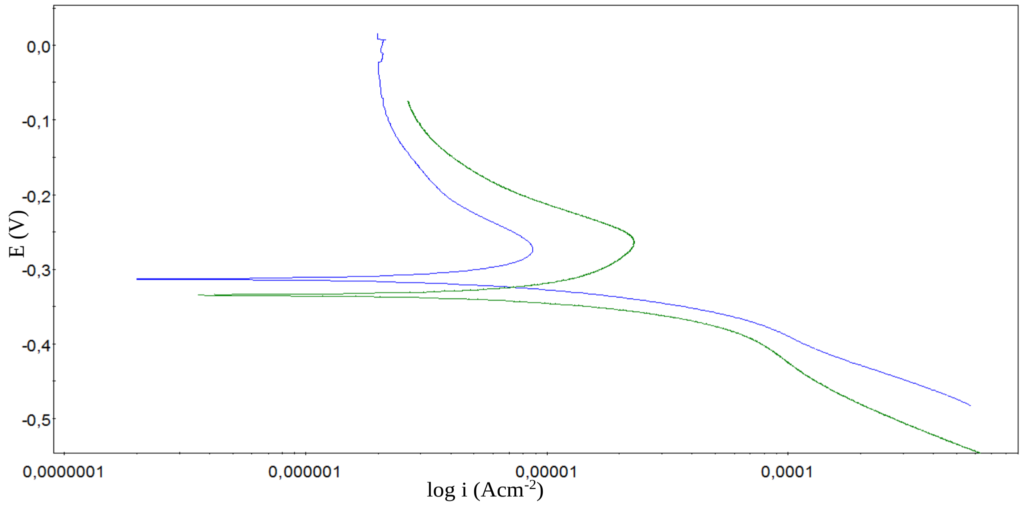

Figure 8. Tafel curves of samples tested in 1 % HCl at 30 °C (---- 317 L, ---- 304 L)

The results shown in Tables 2 and 3 but also Figures 5, 6, 7 and 8 almost undoubtedly show a higher general corrosion resistance of stainless steel type 317 L compared to stainless steel type 304 L.Samples of stainless steel type 317 L at all tested temperatures, 20 °C, 30 °C and 40 °C, as well as in both tested HCl solutions, 0.5% HCl and 1% HCl, show lower values of corrosion current density $i_{cor}$and more positive values of open circuit potential $E_{(I=0)}$ in relation to stainless steel samples of type 304 L.The only exception is the more positive value of the open circuit potential $E_{(I=0)}$ of the stainless steel sample of type 304 L compared to the sample of stainless steel of type 317 L testing of general corrosion of the mentioned stainless steels at temperature 30 °C in 0.5% HCl solution, Table 3 and Figure 7.

The reason for the increase in corrosion resistance of 317 L stainless steel compared to 304 L stainless steel, looking at their chemical composition, should be the content of molybdenum in 317 L stainless steel, because the main difference between them is the absence of molybdenum in 304L.Generally, the addition of molybdenum increases corrosion resistance of wrought austenitic stainless steels [11].Addition Mo to austenitic stainless steels allows formation of a passive film consisted of a solid solution of Mo^{6+} in chromium oxyhydroxide network, which reduces the corrosion current density in the active region for acidic solution [12].

The beneficial effects of molybdenum have been interpreted as follows: molybdenum eliminates the active surface sites through the formation of molybdenum oxy-hydroxide or molybdate on these site, on which it is difficult to form the stable passive film. This leads to the appearance of a homogeneous steel surface and to the formation of a homogeneous passive film [13].In the end, Pourbaix diagrams establish MoO_3 as the only compound formed in strongly acidic media [14].

4. CONCLUSION

Testing the influence of temperature of the HCl solution, HCl concentration and molybdenum content on the rate of general corrosion of austenitic stainless steels, it is concluded:

- With an increase in the concentration of the HCl solution, there is an increase in the rate of general corrosion for both types of stainless steels, 304 L and 317 L.
- With increasing temperature of the HCl solution there is an increase in the rate of general corrosion for both types of stainless steels 304 L and 317 L.
- Higher general corrosion resistance of stainless steel type 317 L compared to stainless steel type 304 L. The reason for the increase in corrosion resistance of 317 L stainless steel compared to 304 L stainless steel, looking at their chemical composition, should be the content of molybdenum in 317 L stainless steel, because the main difference between them is the absence of molybdenum in 304 L. Generally the conclusion can be that the addition of molybdenum increases corrosion resistance of austenitic stainless steels.

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IZVOD

ISPITIVANJE OPŠTE KOROZIJE AUSTENITNOG NERĐAJUĆEG ČELIKA TIPOVI 304 L I 317 L, POSEBNO SA ASPEKTA NJIHOVOG HEMIJSKOG SASTAVA

Austenitni nerđajući čelici su među najčešće korišćenim vrstama nerđajućeg čelika. Najčešće korišćene klase su legure serije 300 Američkog instituta za gvožđe i čelik (AISI). Počevši od osnovne legure 304 (Fe-19Cr-10Ni), dodaje se molibden radi poboljšanja otpornosti na piting (2-3 tež.% kod tipa 316 i 3-4 tež.% kod tipa 317). Preosetljivost usled trošenja hroma tokom zavarivanja i drugih toplotnih tretmana, kao i moguća rezultujuća intergranularna korozija, može se izbeći upotrebom niskougljeničnih razreda (304L, 316L, 317L, u kojima je ugljenik ograničen na 0,03 tež.% mak.) ili dodavanjem titanijuma (tip nital47bium) i hroma (tip nital47 i 321). taloži ugljenik na višim temperaturama. Dodatak hroma takođe daje veću otpornost na oksidaciju, dok nikl poboljšava duktilnost i obradivost materijala na sobnoj temperaturi.

U ovom radu je ispitivana opšta korozija austenitnih nerđajućih čelika, posebno niskougljeničnih tipova 317 L i 304 L. Rezultati istraživanja su predstavljeni u obliku Tafel polarizacionih krivulja, izraženih kroz gustinu struje korozije i potencijal otvorenog kola. Rezultati pokazuju da se brzina opšte korozije ispitivanih austenitnih nerđajućih čelika smanjuje snižavanjem temperature rastvora HCl, smanjenjem koncentracije HCl i prisustva molibdena u sastavu čelika tipa 317 L.

Ključne reči: *austenitni nerđajući čelici, opšta korozija, 317 L, 304 L, Tafelove polarizacione krive*

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