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Araştırma Makalesi / Research Article

The Electrochemical Synthesis of Ferritic Stainless Steel Alloyed With Nb in H_2SO_4 Environment

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Abstract
The current paper, the corrosion behaviors of three types stainless steel alloys with particular Nb element rates synthesized to determine the influence of Nb amount. Niobium is stabilizing element for steels. Besides niobium has higher affinity than chromium. So niobium prevents chromium depletion by making niobium carbide. Niobium microalloying is helpful procedure in order to control recrystallization of steel. Niobium microalloying is related on grain refinement. FSS samples were unalloyed and alloyed with 0.5 and 1% Nb samples. Unalloyed sample is referance sample. The specimens are casting and then forging products. Different heat treatments were applied to samples because of homogenization. The samples were exposed the sulphric acid solution. Ferritic stainless steel (FSS) electrodes were analyzed using electrochemical impedance spectroscopy (EIS). The experiments were performed using with three electrodes system at room temperature. The corrosion product morpholgy on the surface tests of specimens was investigated with SEM. SEM micrographs showed that the samples exposed the generalized pitting in the solution. Corrosion rate was accounted by Stearn-Geary equation. It was observed that both niobium alloying and heat treatment for 30 minutes is increased oxidation resistance of ferritic stainless steel to pitting corrosion. The results indicated that niobium reinforced the passif layer.

Keywords: Ferritic stainless steel, niobium, corrosion, electrochemical synthesis.

Farklı Miktarlarda Niyobyum ile Alaşımlandırılmış Ferritik Paslanmaz Çeliğin Sülfürik Asitte Elektrokimyasal Sentezi

Bu çalışmada, Nb miktarının etkisini belirlemek için belirli oranlarda Nb elementine sahip üç tip paslanmaz çelik alaşımın korozyon davranışları sentezlenmiştir. Niyobyum, çelikler için stabilize edici elementtir. Ayrıca niyobyum, kromdan daha yüksek afiniteye sahiptir. Bu yüzden niyobyum, niyobyum karbür yaparak tane içinde krom fakirleşmesini önler. Niyobyum mikroalaşım, çeliğin yeniden kristalleşmesini kontrol etmek için kullanılan yararlı bir prosedürdür. Niyobyum mikroalaşım, tane inceltme ile de ilgilidir. FSS numuneleri alaşımsızdır ve %0.5 ve %1 Nb numuneleri ile alaşımlanmıştır. Alaşımsız numune, referans numunedir. Numuneler döküm ve dövme ürünüdür. Homojenizasyon elde etmek için numunelere farklı ısıl işlemler uygulanmıştır. Numuneler sülfürik asit çözeltisine maruz bırakılmıştır. Ferritik paslanmaz çelik (FSS) elektrotları, elektrokimyasal empedans spektroskopisi (EIS) kullanılarak analiz edilmiştir. Testler, oda sıcaklığında üç elektrotlu sistem kullanılarak yapılmıştır. Numune yüzeylerindeki korozyon ürünlerinin morfolojisi SEM ile incelenmiştir. SEM mikrografları, numunelerin çözelti içinde çukurcuk korozyonuna uğradığı görülmüştür. Korozyon hızları Stearn-Geary denklemi ile hesaplanmıştır. Hem niyobyum alaşımının hem de 30 dakikalık ısıl işlemin, ferritik paslanmaz çeliğin çukurcuk korozyonuna karşı korozyon direncini arttırdığı gözlemlenmiştir. Sonuçlar, niyobyumun pasif tabakayı güçlendirdiğini göstermiştir.

Anahtar kelimeler: Ferritic paslanmaz çelik, niyobyum, korozyon, ferritik paslanmaz çelik.

1. Introduction

There are three main types stainless steels austenitic, martensitic and ferritic Austenitic and ferritic SS have the best corrosion resistance among these steels. Steels have been used in a lot of industrial

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applications. The consistence of oxide film and its repassivation kinetics can be improved by means of alloying elements. The decay of the passive layer can begin by means of alchemical or machine-driven attack in acidic environment resulting in the localized corrosion [1,2]. To improve corrosion behavior of the SS, the natural reaction of Cr and Fe on the outside to form passive layers consisting of both oxides and hydroxides is an significiant agent [3]. There are a few methods. Alloying is a favorite method. The best alloying elements for stainless steels are Nb, Mo, Ti, V and W due to their stabilizer properties. The efficacy of Sn on corrosion rate of FSS in was analyzed by electrochemical methods and gravimetric tests at 25°C [4]. Tribocorrosion activity of AISI 4340 ferric SS flowing against alümina in 0.5 M H_2SO_4 has been checked employing a system of electrochemical measure [5]. The effect of Nb alloying is tested on the electrochemical activity of low-alloy steel using EIS in H_2SO_4 environment.[6]. Bojinov et.all.[7] found an addition of the electric circuit archetype to estimate the electrochemical action of anodic layers on unalloyed steel alloys in 1 M H_2SO_4 environment. Super 304H ASS were studied by polarization tests having dynamic and static character and surface analysis in order to determine effects of Nb and media temperature on pitting corrosion [8]. The corrosion behavior of 304L type SS was investigated in a unaired 1M H_2SO_4 solution [9]. Irani and Ghazani investigated the influence of grain refiment on electrochemical behavior of 18.5 % Cr ferritic stainless steel. They found that the refining grain has goor effect on the samples [10]. 430 ferritic stainless steel in concrete was investigated. It was presented some measurements [11]. In other study, Fe-20Cr alloy was tested in 1 M H_2SO_4 at 30°C. Resistance of rotective layer was observed using Mott-Scotty analysis [12]. Luo at all. investigated 316L stainless steel in calcium hydroxide and potassium hydroxide solutions. They found that 316L stainless steel has resistance to pitting corosion [13]. Xu at all observed corrosion behavior and oassive layer features of 304 stainless steel in high temperature solutions. They discussed the corelation between these phemomeno [14].

Niobium is one of alloying elements extensively used due to properties improving corrosion and mechanical properties of steels. One of the major benefits of Nb is to prevent intergranular corrosion forming carbides before chromium. This occurs at 550–800°C. Intergranular corrosion and intergranular stress corrosion cracking arise from sensitization basically [15-20]. Bai et all. [21] investigated effect of niobium on 304 stainless steel in 60 % nitric acid media.

This paper presents the effect niobium element in enhancing corrosion resistance comparison with unalloyed stainless steel. Besides, it shows the effect of heat treatment and presents knowledge faithfulness of EIS.

2. Material and Method

2.1. Materials

The specimens are 12Cr ferritic stainless steel. Table 1 shows the elemental analysis of samples. It has been constituted three sets: The first set is without heat treatment, the second set was exposed for 30 minutes and third set was exposed for 180 minutes at 1100°C. Then they were quenched. The samples were exposed to 1200 grid silicon paper. The electrochemical tests were realized in a convantional three-electrode device. Reference electrode is Ag/AgCl electrode and counter electrode is Pt foil. FSS is working electrode. The electrochemical investigations was performed with CHI 604 model potentiostat/galvanostat device. Merck mark chemicals are used. SEM phtographies of samples were obtained

Table 1. The spectral analysis of specimens

Sample	Alloy	Elements (wt. %)									
no	Ele.	C	Mn	Si	Cr	Nb(±0.02)	Ti	Mo	V	P	S
S1	FSS	0.048	0.25	0.28	18.21	-	-	-	-	0.02	0.01
S2	.5% Nb	0.054	0.081	0.03	18.15	0.5	-	0.065	0.030	0.030	0.012
S3	1 % Nb	0.052	0.109	0.246	18.06	1	-	0.061	0.026	0.019	0.009
S4	3% Nb	0.053	0.188	0.368	17.64	3	-	0.065	0.136	0.007	0.006

2.2. Electrochemical data

The electrochemical impedance spectroscopy was used as test method. The tests were performed under air and at room temperature. Impulses in EIS datas were applied in the frequencies 10^5-10^{-1} Hz with peak-to-peak AC amplitude of 7 mV. There is equivalent circuit model in Figure 1 [22].

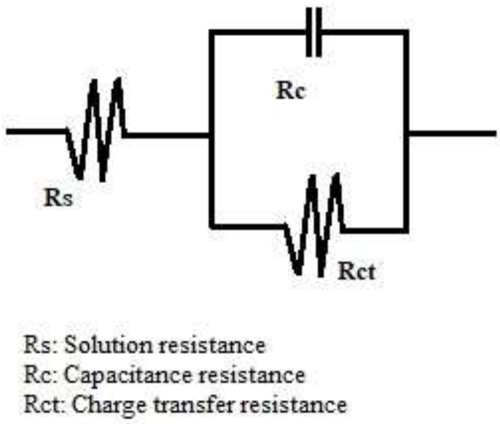


Figure 1. Electrical circuit model of Fe-Cr alloys

3. Results and Discussion

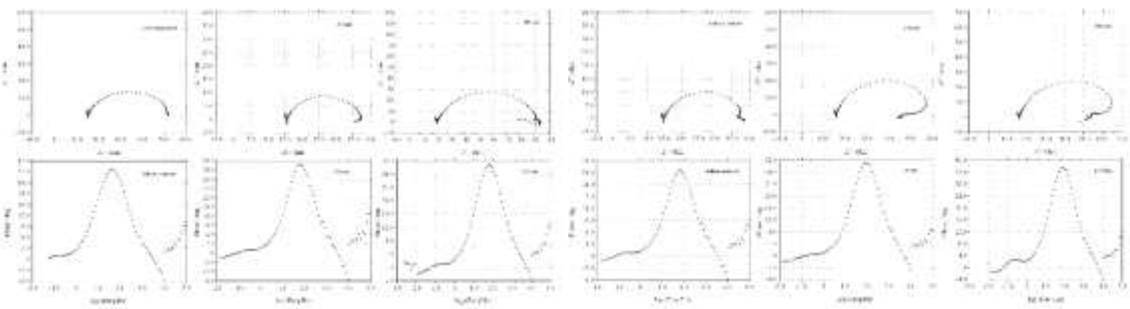
3.1. An overwiev corrosion

Polarizations values are listed in Table 2

Table 2. Polarization parameters of FSS samples in 0.1 M H_2SO_4 acid solution

Samples	Homogenization period	R_p (ohm)	E_{corr} (Volt)	I_{corr} (mAmper)
S1	*a-without*	34.75	-0.520	1.5
	b-½ hour	23.33	-0.504	2.31
	c-3 hours	71.25	-0.527	0.83
S2	*a-without*	23.45	-0.523	2.37
	b-½ hour	34.35	-0.499	2.07
	c-3 hours	48.39	-0.507	1.36
S3	*a-without*	30.80	-0.523	1.89
	b-½ hour	36.34	-0.523	1.44
	c-3 hours	34.85	-0.522	1.68
S4	*a-without*	23.7	-0.501	2.23
	b-½ hour	38.23	-0.520	1.37
	c-3 hours	43.43	-0.519	1.55

Figure 2 shows the variations of the impedance spectra.



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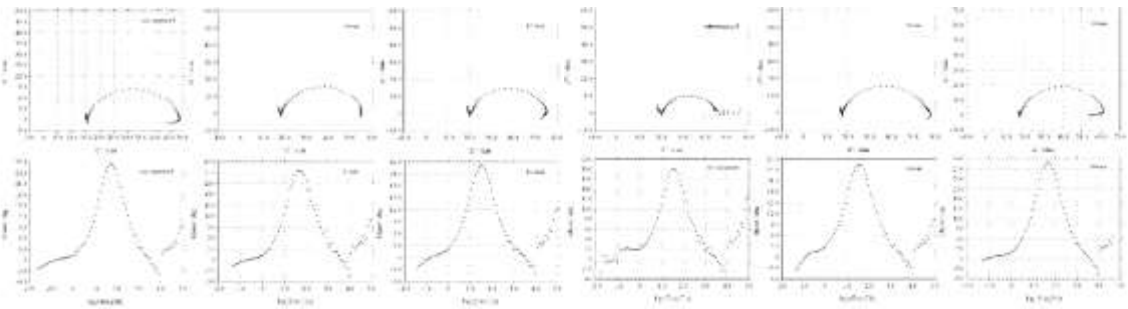

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Figure 2. Variations of impedance spectra and the phase angel (θ)-log freq circles of a-S1 b-S2 c- S3 d-S4 in 0.1 Molar H_2SO_4

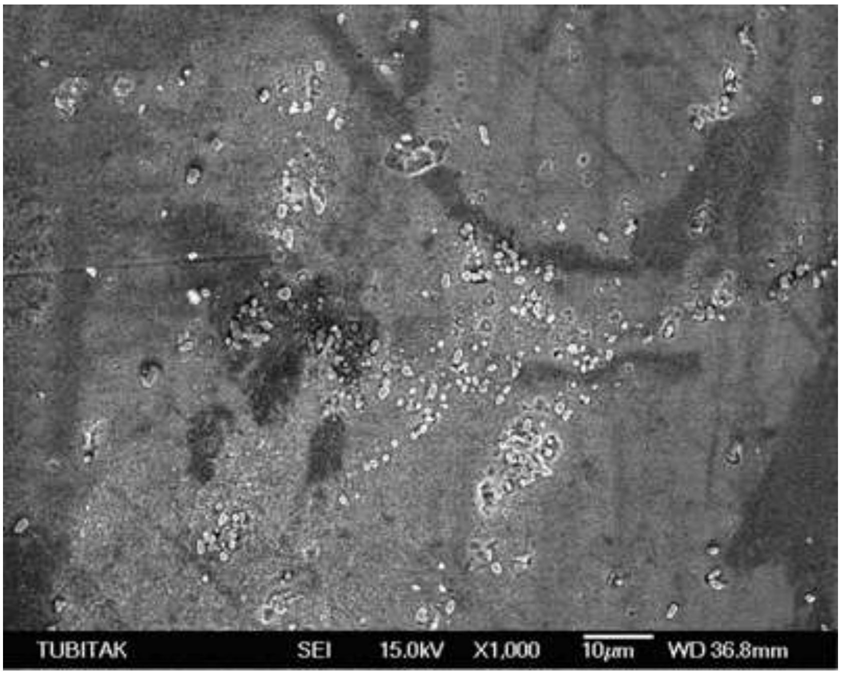

Figure 3. SEM images of S2-b specimen

To obtain polarization resistance (Rp) value used The Nyquist graphics including both charge transfer resistance (Rct) (Fig. 3) and diffuse layer resistance (Rd) [23]. The semicircle in the high frequency region is refer to the impedance of the surface films formed on the surface. Warburg impedance was not seen in low frequencies. The E_{corr} values were obtained as -0.520, -0.504 and -0.527 V in order. The highest phase angel is 1.8 Hz. The heat treatment improved Rp value. When heat treatment period increased the R_p value increased for S1 sample because of protective metal oxide layer formed on the surface. Additionally destroying of oxide layer was prevented by means of removing discontinuities because of heat treatment dissolved $M_{23}C_6$ carbides, as seen in Fig 4.

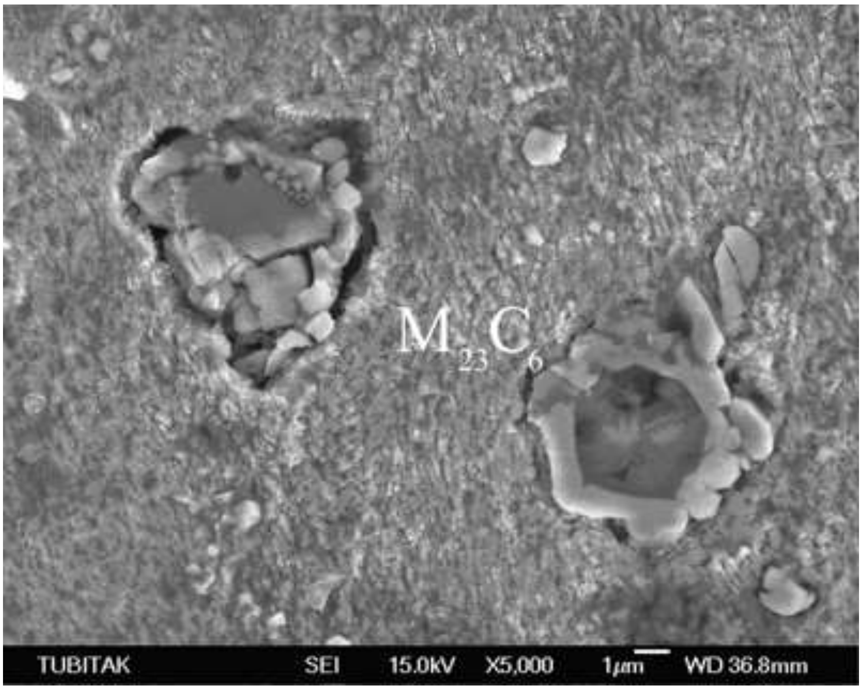

Figure 4. SEM images of sample S3

Nyquist diagrams exhibit semicircular change, as seen from in Fig. 2(b). Free-heat treatment sample S2 has the worst corrosion impedace (23.45 **Ω**) and then resistance rised to 34.35 **Ω** and 48.39 **Ω** as homogenization time increased 30, 180 minutes respectively. This indicates that free-heat treatment sample S2 expose to corrosion because of damaging on its passive layer. In sample S2, the highest phase angel was attained as 2 Hz.

As observed from figure 2c, the type of Nyquist diagrams look like to others. The corrosion resistance of sample is observed at high frequencies and Warburg impedance was not observed at low frequencies region of the diagrams.

Nyquist diagram of sample S4 have semi-ellipse change as seen in Figure 2(d). The sample exposed to heat treatment-180 minutes has ultimate corrosion resistance. Maximum phase angel is 1.6 Hz.

None of samples has Warburg impedance. It can be explained that the corrosion mechanism has not controlled by diffusion and the ion diffusion actualizes toward metal surface on oxide layer. It can be said that the pitting resulted in corrosion damage. Consequently, stable oxides formed by means of oxidizing of metal. These electrochemical processes are following [24]:

$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Nb + H_2O = NbO + 2H^+ + 2e^-$$
$$NbO + H_2O = NbO_2 + 2H^+ + 2e^-$$
$$2NbO_2 + H_2O = Nb_2O_5 + 2H^+ + 2e^-$$

According to Table 2, niobium improved corrosion resistance of free-heat treatment steel samples and exposed to heat treatment FSS electrodes for long period. When niobium amount increased the R_p values increased for samples homogenized for half an hour. Generally, all of the steels have exposed to heat treatment. Because of composed of a lot of elements, they need homogenizationoperation. So, it can be proposed that niobium reduced corrosion rate of ferritic stainless steel.

The value of R_p was obtained from Nyquist diagrams. R_p resistants are used to count the corrosion currents (I_{corr}) from the Stearn-Geary equivalent ($I_{corr} = B / R_p$), the value of B is 52 mV for steel [25, 26].

3.2. Surface analysis

The specimens exposed to homogenization for 30 minutes are analyzed by SEM as seen in Fig. 5. Pitting is observed on the surface of samples. Additionally surface of samples with Nb are more regular surfaces.

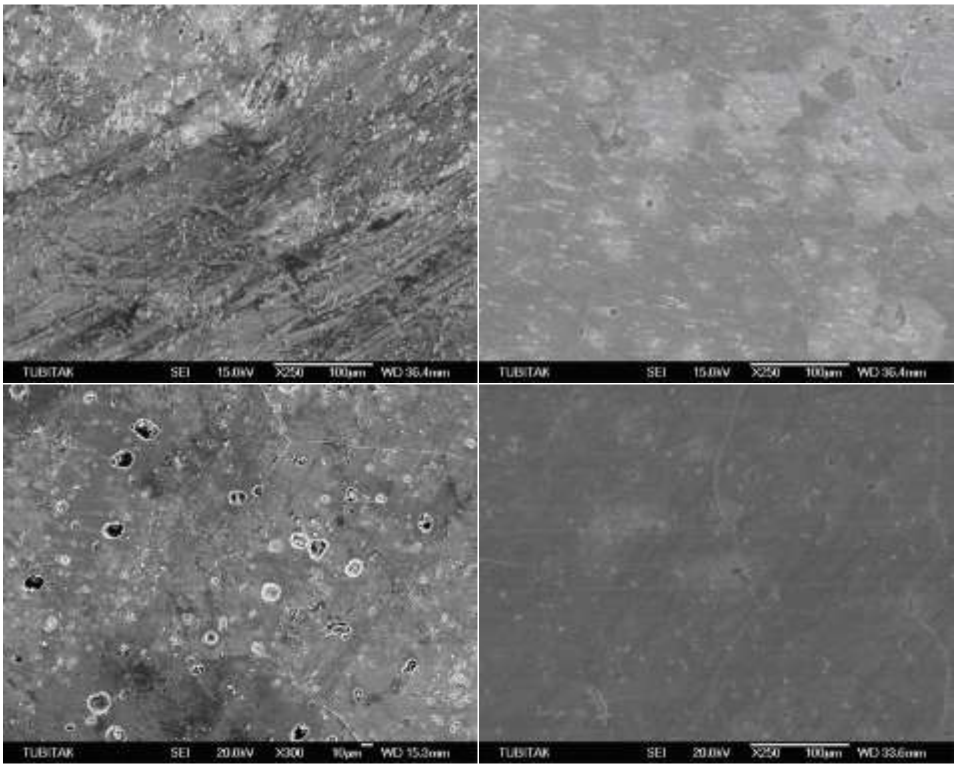

Figure 5. SEM images of samples S1- S4 homogenized for 30 minutes, respectively

According to results of experiment, it was obtained better result samples with niobium. It can be explained that: there is a stable layer on surface of sample. This layer was constituted by niobium. Alonso-Falleiros et. al. [27] and Seo [28] explained the conglomeration of Nb on the superfice during active solution of ferritic steel in H_2SO_4 acidic environment. Niobium element formed niobium oxides, probably. The oxide layer protected the surface. Oxide layer formed by means of Nb has worse protection than that of Cr [29-31].

4. Conclusions

- The Impedance spectroscopy technique (*EIS*) must be preferred to study corrosion of stainless steel. Since the method has given accurate data.
- The stainless steels in sulphuric acid solutions suffered the localized corrosion commonly.
- According to EIS measurements, the addition of niobium has the useful influence of improving the corrosion resistance of the samples since niobium constitutes stable niobium carbide with carbon. Consequently, this prevents depletion of chromium in the matrix and then intergranular corrosion does not occur.
- When niobium amount increased, the R_p values increased for specimens exposed for half an hour.
- Pitting corrosion was determined on the surface of samples.

Author's Contributions

The entire work was done by the author

Statements of Conflicts of Interest

The author has no conflict of interest regarding this article.

Statement of Research and Publication Ethics

The author declares that this study complies with Research and Publication Ethics.

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