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ORIGINAL PAPER

Corrosion behavior of ferritic stainless steel alloyed with different amounts of niobium in hydrochloric acid solution

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Abstract The corrosion behavior of stainless steel alloys containing corrosion-resistant elements was investigated. Ferritic stainless steel (FSSs) electrodes were synthesized by applying a scan rate of 1 mV s^{-1}. Stainless steels were used unalloyed and alloyed with about 0.5, 1, and 3 wt% elemental Nb. The samples were obtained from casting and forging. The samples were classified into three groups. In the first group, samples were unhomogenized and remained in production condition. In the second and third groups, samples were exposed to homogenization at 1,100 °C for 30 min or 180 min, respectively, and then quenched. The corrosion performance of the FSSs was investigated in 0.3 M HCl acid solution using electrochemical impedance spectroscopy (EIS). Corrosion resistance was calculated using the Stearn–Geary equation. SEM investigations of samples immersed in 0.3 M HCl acid solution for 60 and 360 min were performed. SEM micrographs showed generalized pitting. Consequently, it was determined that niobium has a beneficial effect on the corrosion resistance of FSS since niobium reacts with carbon to form stable carbides.

Keywords Electrochemical impedance spectroscopy · Ferritic stainless steel · Nyquist diagram · Hydrochloric acid solution

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1 Introduction

Stainless steels have been used in various ways due to their properties such as strength, corrosion resistance and formability. Ferritic stainless steels (FSSs) are iron-based alloys containing between 10.5% and 30% Cr. The cost of FSS is lower than that of austenitic stainless steel and, consequently, the use of FSS, represented by type 430, has been increased. They have microstructures consisting of ferrite plus carbide.

The high corrosion resistance of ferritic steels with a chromium content of 13–30% has long been well known [1].The principal problem with FSSs is sensitization, which occurs due to formation of either chromium carbides or nitrides at grain boundaries. Their formation leaves a zone depleted of chromium around the carbides that makes the steel susceptible to intergranular oxidation. Adding other elements that scavenge the carbon and nitrogen solves this problem. An investigation of the influence of additional alloying elements on the corrosion behavior of FSSs is an important subject for further investigation [2]. The influence of alloying elements on corrosion resistance is related to the stability of the passive film and its repassivation kinetics. It is believed that the stability of the passive films and their repassivation kinetics are subject to the influence of metallurgy, applied repassivation potentials, pH and chloride ion concentration in aqueous solutions [3–9].

Stainless steel is composed of many grains, phases and other heterogeneities, such as non-metallic inclusions. Accordingly, new electrochemical techniques are needed to investigate the effects of alloying elements.

In recent years, niobium has been studied as a very effective alloying element to improve the properties of steels. Niobium has high mechanical and corrosion resistance in acidic solutions. In most aqueous solutions that are usually considered to be highly corrosive environments, Nb stability is due to a natural oxide film on its surface.

Numerous papers have been published concerning the effect of Nb on steels. However, the effects of both Nb and heat treatment on the electrochemical behavior of FSS have not been thoroughly investigated. The present work investigates the role of carbide formation with niobium in enhancing the corrosion behavior of FSS when compared with unalloyed steels by evaluating its corrosion resistance and corrosion morphology. Additionally, the effects of heat treatment on the corrosion behavior of FSS were investigated and the corrosion performance of this steel was investigated in 0.3 M HCl acid solution.

2 Experimental

2.1 Sample, electrochemical equipment and chemicals

In this study 12% Cr FSS specimens were used. The chemical compositions (wt%) are given in Table 1. The samples were classified into three groups. The first group was unhomogenized, the second was homogenized for 30 minutes at 1,100 °C, and the third group was homogenized for 180 minutes at 1,100 °C, followed by water quenching. Before the experiment the specimens were polished with 1200 grit silicon paper until the surface appeared to be free of scratches and other defects.

Electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was Ag/AgCl, and the counter electrode was a platinum sheet of surface area 10 mm × 20 mm. All electrode potential values are referred to this reference electrode. The working electrodes were FSS samples (with and without Nb) with 10 mm × 10 mm of electrode area embedded in epoxy resin.

A CHI 604 model computer-controlled electrochemical analyzer was used for impedance measurements. All chemicals were analytical grade from Merck and were used as received. An Oxford Inca system attached to a JEOL JSM-6335-F scanning electron microscope was used for microstructure, phase and recrystallization analyses.

Table 1 The chemical compositions of samples (wt%)

Chemical composition/wt%	Samples			
	S1	S2	S3	S4
C	0.048	0.045	0.082	0.077
Mn	0.250	0.081	0.109	0.188
Si	0.280	0.03	0.246	0.368
Cr	18.21	18.15	18.06	17.64
Nb(±0.02)	–	0.5	1	3
Mo	–	0.065	0.061	0.065
V	–	0.030	0.026	0.136
P	0.020	0.030	0.019	0.007
S	0.010	0.012	0.009	0.006

2.2 Electrochemical measurement

Electrochemical impedance spectroscopy was used to investigate the corrosion performance of the alloys. Impedance measurements were carried out at the open circuit potential (E_{oc}) using a computer-controlled analyser. Prior to the impedance measurement, a stabilisation period of 30 min was allowed, which proved to be sufficient to attain a stable value for E_{oc}. The Nyquist plots were obtained with potential waves of 7 mV amplitudes around the corrosion potential, with frequencies ranging from 10^5 to 10^{-1} Hz.

3 Results and discussion

3.1 Corrosion tests

The corrosion performance of niobium-alloyed and unalloyed FSS was investigated in 0.3 M HCl acid solution. Values of R_p, E_{corr} and I_{corr} are given in Table 2.

The Nyquist diagrams and phase angle (θ)-log freq curves for FSSs both with and without niobium are given Fig. 1.

This shows depressed semicircles; the diameters of these curves are equal to the polarization resistance (R_p). This includes the charge transfer resistance (R_{ct}) corresponding to the metal/solution interface formed at the bottom of the pores (Fig. 2), the oxide film resistance (R_o) and the diffuse layer resistance (R_d) [10, 11]. Warburg impedance was not

Table 2 R_p (Ω), E_{corr} (V), I_{corr} (mA) values of FSS electrodes after various heat treatment times in 0.3 M HCl acid solution

Samples	Heat treatment (time/min)	R_p (Ω)	E_{corr} (V)	I_{corr} (mA)
S1	Unhomogenized	25.74	−0.497	2.04
	30 min	27.46	−0.491	1.95
	180 min	95.78	−0.502	0.54
S2	Unhomogenized	27.32	−0.497	2
	30 min	68.3	−0.493	0.76
	180 min	73.34	−0.5	0.72
S3	Unhomogenized	37.79	−0.494	1.6
	30 min	75.01	−0.494	0.79
	180 min	94.58	−0.495	0.55
S4	Unhomogenized	25.19	−0.492	2.34
	30 min	69.2	−0.481	0.78
	180 min	77.18	−0.498	0.71

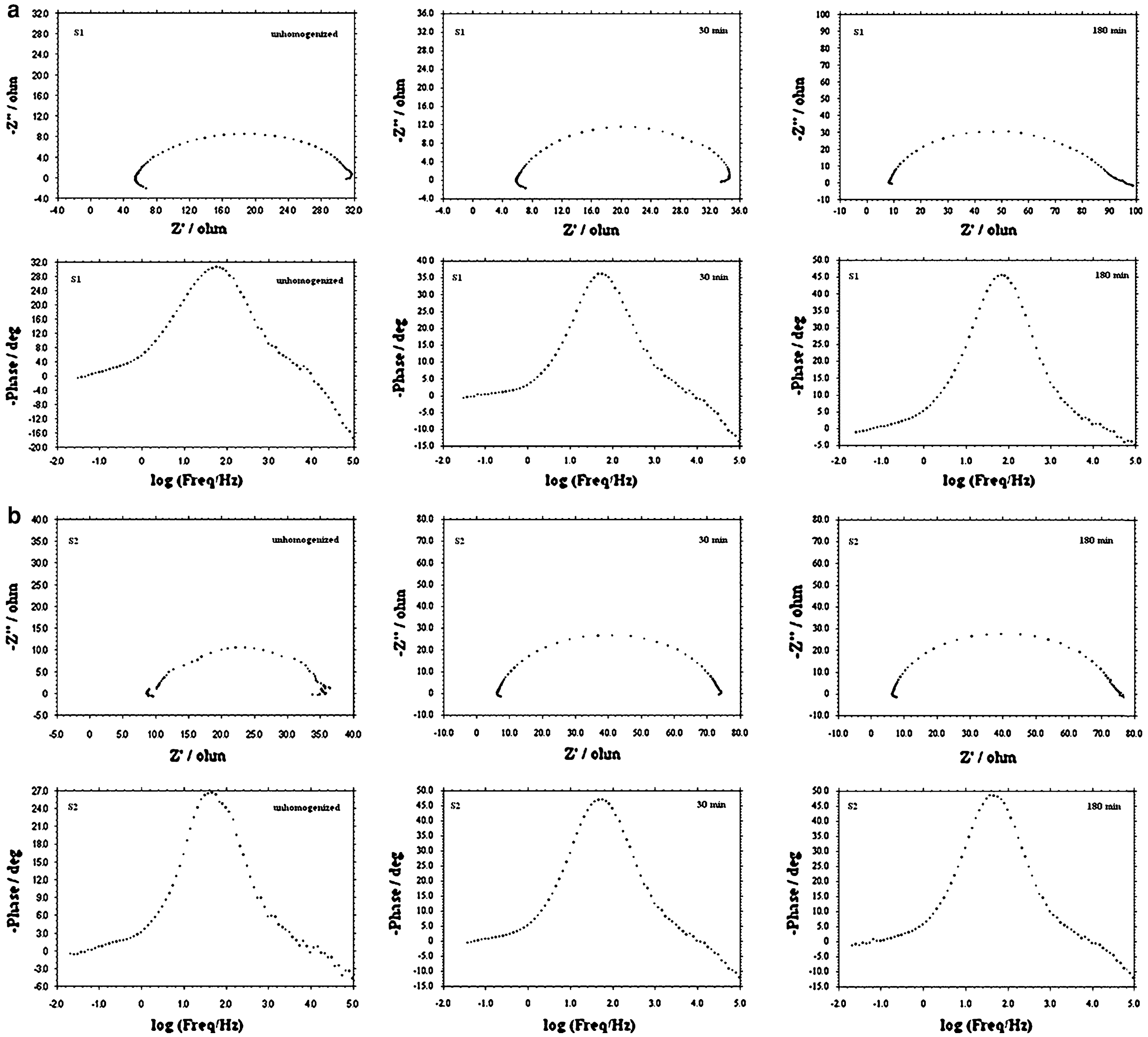

Fig. 1 The Nyquist diagrams and the phase angle (θ)-log freq curves obtained for samples **a**—S1 **b**—S2 **c**—S3 **d**—S4 in 0.3 M HCl; unhomogenized, homogenized for 30 and 180 min

evaluated for all the samples. Under these conditions, there was no possibility for passive film formation on the surface.

As seen in the Nyquist diagrams of sample S1 in Fig. 1a, the measured E_{corr} values were −0.497, −0.491 and −0.502 V in sample S1, respectively. The maximum phase angle was 2 Hz, but the $\mathrm{R_p}$ value increased further with homogenizing heat treatment. The highest R_p value was obtained from sample S1, which was homogenized for 180 min. This case is simply explained by the formation of a protective MeO layer on the surface. The heat treatment dissolved the $M_{23}C_6$ carbides; thus, the discontinuities that destroyed the oxide layer were removed. This case can be seen in Fig. 3. The R_p value was very low in the unhomogenized sample S1. This may be explained by the inner structure and other internal stresses. There is a region around the carbides where internal stress and energy levels are the highest. In this region there is alloy segregation and the corrosion rate is high. The corrosion resistance of samples S1, S2, S3 and S4 improved after heat treatment for 180 min.

As seen in Fig. 1b, the Nyquist diagrams of sample S2 exhibit semicircular change. Unhomogenized sample S2 had the lowest resistance (23.45 Ω), and this value increased to 34.35 and 48.39 Ω when heat treatment was applied for 30 and 180 min, respectively. This indicates

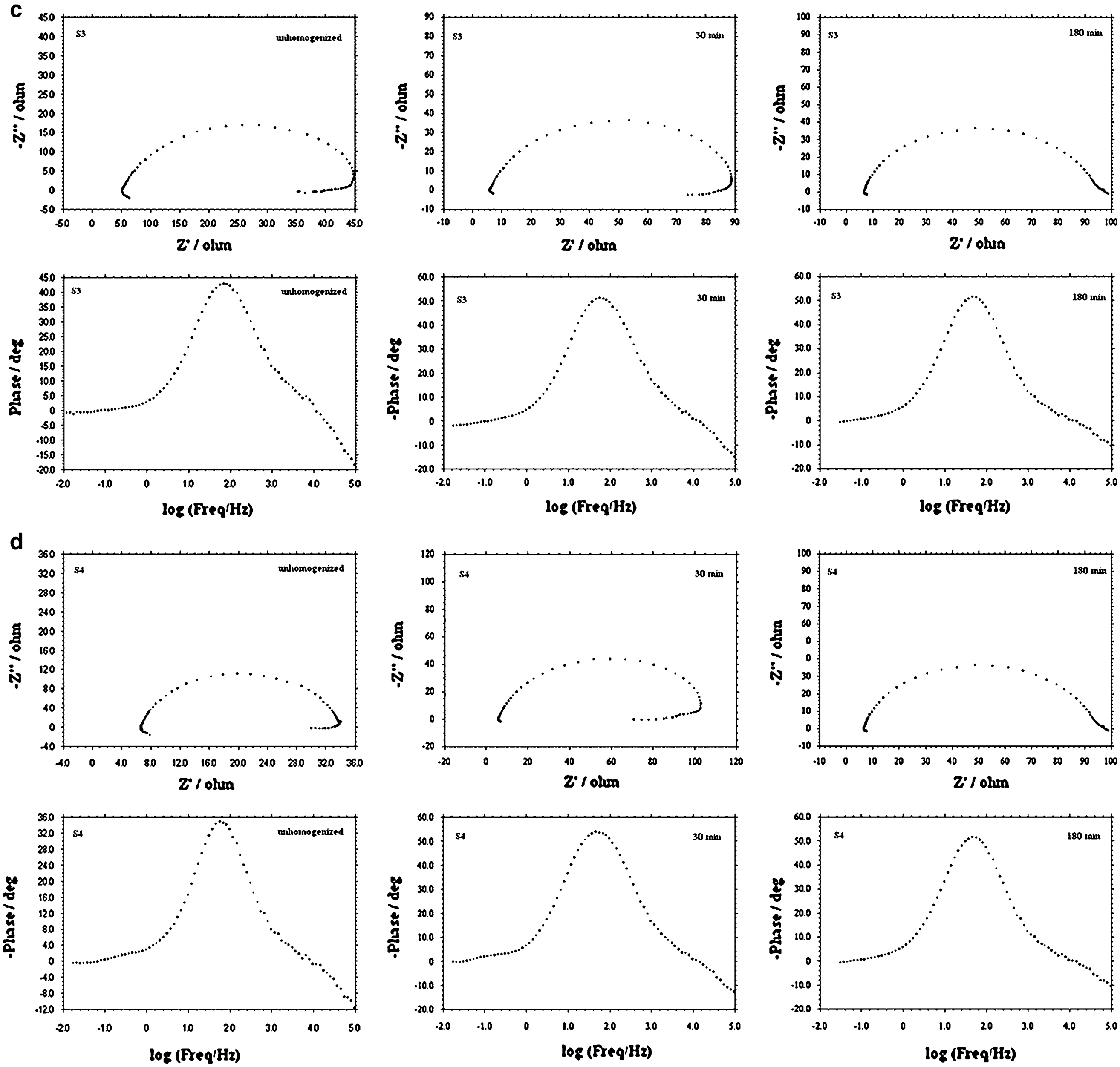

Fig. 1 continued

that the unhomogenized sample S2 suffered severe damage to its passive layer. The corrosion resistance of S2 homogenized for 180 min was lower than that of sample S1. Nb-containing samples have NbC and Nb_2C carbides in addition to σ phase, inclusions and $M_{23}C_6$ carbides. In sample S2 the maximum phase angle was 2 Hz.

As seen in Fig. 1c, the shape of the Nyquist plots for sample S3 is similar for different heat treatments. At high frequencies, a semicircle attributable to the charge transfer (R_{ct}) process was observed and at lower frequencies no linear part (Warburg impedance) was observed. This charge transfer resistance (R_{ct}) is at the metal/film interface. The corrosion resistances were 37.79, 75.01 and 94.58 Ω. Additionally, heat treatment for 180 min improved the corrosion resistance. Increasing the amount of niobium also increased the corrosion resistance as it is known that Nb spontaneously forms passive films.

As seen in Fig. 1d, the Nyquist diagrams of sample S4 show semicircular shape. The highest corrosion resistance was observed in the sample homogenized for 180 min. The maximum phase angle was 1.6 Hz. Increasing the amount of niobium to 3 wt% decreased the corrosion

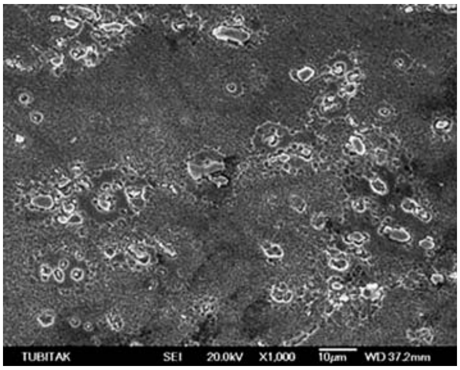

Fig. 2 SEM photography of sample S4 unhomogenized

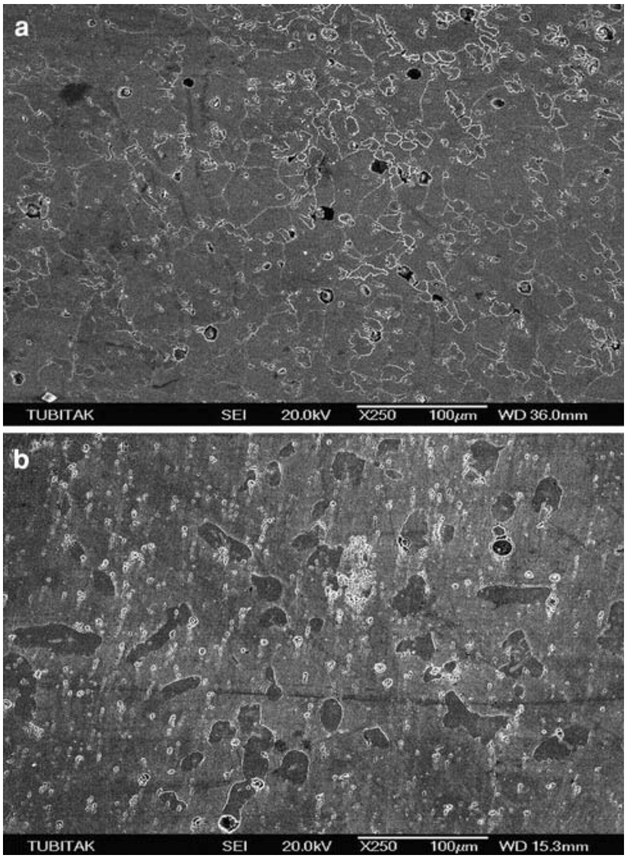

Fig. 3 SEM photographs of sample S1 **a**—unhomogenized, **b**—homogenized for 180 min

resistance. Among the samples homogenized for 180 min, the corrosion resistance was the lowest in this case. This can be attributed to an increasing level of niobium in the matrix, which causes disorders that lead to corrosion. Additionally, Nb encourages a σ phase so the corrosion rate increases.

Warburg impedance was not observed in any of the Nyquist diagrams. It was concluded that the system was not diffusion controlled and that ion diffusion occurred through the oxide layer toward the metal surface. The corrosion process starts from the bottom of the pores. Consequently, the metal is oxidized, thereby yielding stable oxides. The electrochemical processes are given below [12]:

$$\text{Anodic reaction} \quad : \quad \mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-} \tag{1}$$

$$\underline{\text{Cathodic reaction} \quad : \quad {}^{1}\!/_{2}\,\mathrm{O}_2 \pm \mathrm{H}_2\mathrm{O} \pm 2\mathrm{e}^{-} \rightarrow 2\mathrm{OH}^{-}} \tag{2}$$

$$\text{Total reaction} \quad : \quad \mathrm{Fe} + {}^{1}\!/_{2}\,\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(OH)}_2. \tag{3}$$

If there is sufficient oxygen in the environment, iron 2-oxides convert to iron 3-oxides by the following equation:

$$2\mathrm{Fe(OH)}_2 + {}^{1}\!/_{2}\,\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{Fe(OH)}_3. \tag{4}$$

As shown in Table 2 niobium has a deleterious effect on the corrosion resistance of unhomogenized FSS electrodes and FSS electrodes that have been homogenized for 180 min. The R_{p} values start to increase with increasing niobium amounts for samples homogenized for 30 min. The steels were not used without heat treatment, so it can be stated that niobium increases the corrosion resistance of FSS.

The Nb on the electrode surface is always covered by a natural oxide film, predominately $\mathrm{Nb_2O_5}$ as the outer layer and a small portion of $\mathrm{NbO_2}$ as the inner layer, as seen in Eq. 5 [13].

$$2\mathrm{NbO}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Nb}_2\mathrm{O}_5 + 2\mathrm{H}^{+} + 2\mathrm{e}^{-}. \tag{5}$$

The value of R_{p} was determined by extrapolation of the Nyquist diagrams. R_{p} values were used to calculate the corrosion current (I_{corr}) values using the Stearn–Geary equation ($I_{\mathrm{corr}} = B/R_{\mathrm{p}}$). The value of B was 52 mV for all samples [14, 15].

3.2 Results of immersion test

Scanning electron micrographs of FSS exposed to heat treatment for 30 min are shown in Fig. 4. Generalized pitting is evident. The latter samples showed a more regular surface with the addition of niobium.

Samples with niobium gave better results. This can be explained by the presence of a stable surface layer. The accumulation of Nb on the surface of ferritic steel during immersion in sulfuric acid solution was confirmed by Neuso and Wolynec [16] and Seo et al. [17]. Elemental niobium most likely formed niobium oxides, which protect the surface. Protection by the oxide layer formed by Nb is stronger than the protection of chromium oxides [18–20].

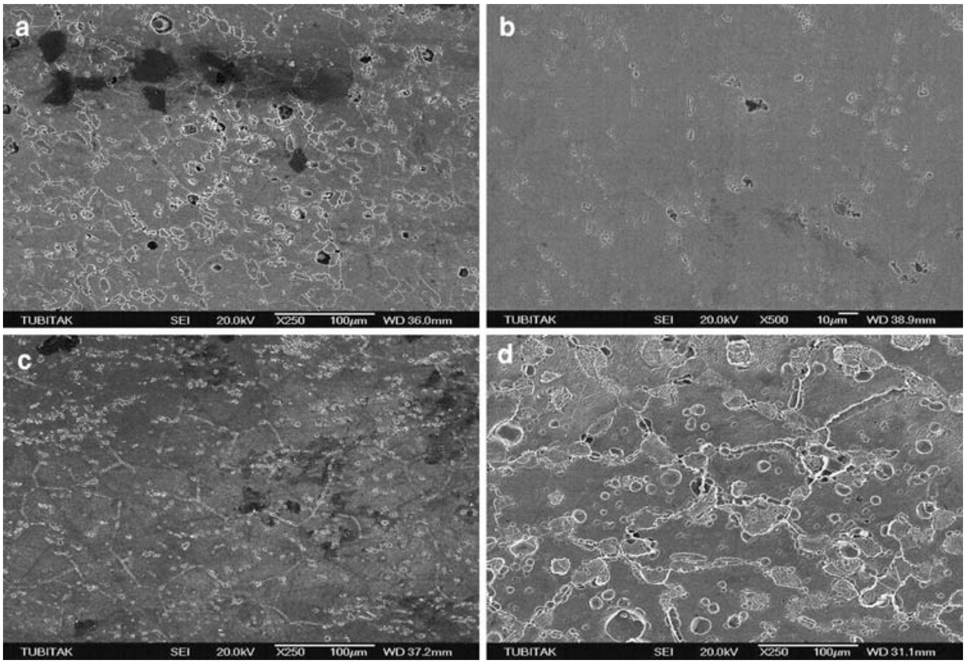

Fig. 4 SEM micrographs of samples **a**—S1, **b**—S2, **c**—S3 and **d**—S4 homogenized for 30 min

4 Conclusions

- Impedance spectroscopy (EIS) is a powerful technique for the investigation of corrosion protection in stainless steel.
- Localized corrosion is a serious problem for stainless steels when they are exposed to hydrochloric acid solutions.
- The addition of niobium improves the corrosion resistance of FSS since niobium reacts with carbon to form stable carbides. This results in the maintenance of an effective content of chromium in the matrix.
- According to EIS measurements increasing the Nb content results in increased corrosion resistance of FSSs in HCl acid solution.
- Niobium is known to be more effective at improving the high temperature strength of steel. The high temperature strength is largely dependent on the amount of matrix and precipitation, as well as grain size. In this study, matrix and precipitation are considered decisive factors since homogeneity and stable microstructure are very important for corrosion resistance. It is suggested that dissolved niobium is effective in improving corrosion resistance. The amount of dissolved niobium depends on the annealing temperature and time.
- Satisfactory results were obtained from a sample homogenized due to the removal of structures that cause corrosion. The R_p values started to increase with increasing niobium amounts for samples homogenized for 30 minutes.
- It was observed that generalized pitting is evident on the samples.
- The best localized corrosion resistance was obtained from the alloy containing 1 wt% niobium among the samples homogenized for 30 min. A homogenizing heat treatment for 30 min has a useful effect on the corrosion resistance of Nb-containing samples.
- Because Nb-containing samples demonstrated similar corrosion resistance, different niobium amounts that are compatible with the carbon content of the steel should be investigated.

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