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Electrochemical Impedance Spectroscopy Study of the Corrosion Behavior of Some Niobium Bearing Stainless Steels in 3.5% NaCl

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Electrochemical Impedance Spectroscopy (EIS) is a powerful, rapid and accurate non-destructive method for the evaluation of wide range of materials. In this work, the corrosion behavior of some austenitic stainless steels was studied in 3.5%NaCl. The effect of Nb content and cold deformation on the corrosion resistance was investigated. The occurrence of localized corrosion due to chloride ion attack was examined by visual inspection and SEM-EDS. XRD analysis was used to identify the chemical composition of the outer oxide layer. According to EIS, the corrosion resistance increased by increasing the Nb content. Cold deformation (CD) has a critical effect on the corrosion resistance. The specimens prepared at 23% CD showed the best corrosion resistance. The surface resistance increased double compared with that without CD. Increasing the deformation to 40% and 50% affects negatively the corrosion resistance. XRD reveled presence of Cr-rich film in the specimen bearing the highest Nb-content. It is argued that increasing the Nb-content enhancing formation of surface film enriched with Cr and Ni which has a high corrosion resistance.

Keywords: Corrosion, Niobium Bearing Stainless Steels, Electrochemical Impedance Spectroscopy, Sodium Chloride

1. INTRODUCTION

Electrochemical Impedance Spectroscopy (EIS) has many advantages in comparison with other electrochemical techniques. During EIS experiments, a small amplitude ac signal is applied to the system being studied. Therefore, it is a non-destructive method for the evaluation of a wide range of materials, including coatings, anodized films and corrosion inhibitors. It can also provide detailed information of the systems under examination; parameters such as corrosion rate, electrochemical mechanisms and reaction kinetics, detection of localized corrosion, can all be determined from these data.

Austenitic stainless steels are the most popular metallic materials because of their relatively low cost, ease of fabrication and reasonable corrosion resistance [1, 2].

One of the main disadvantages of stainless steels is the problem of localized corrosion when they are exposed to chloride solutions [3-5]. There are several surface modification techniques to improve stainless steels' behavior against localized corrosion in such media. One of them is addition of alloying elements such as Mo, Ni, V, Si [6, 7-11].

Nb alloying element is added to austenitic stainless steels to enhance the mechanical properties at high temperatures. The presence of Nb increases the proof strength of austenitic stainless steels even at high temperatures [12].

One of the main advantages of Nb is to avoid sensitization – a process by which chromium carbides form at grain boundaries with adjacent depletion of chromium [13–15]. This happens at the temperature range of 550–800 °C such as during welding. Sensitization is the basic reason for intergranular corrosion and intergranular stress corrosion cracking [16].

Cold deformation of austenitic stainless steel is unavoidable for the fabrication of components. Several investigations carried out in the past have reported unclear role of cold working on the localized corrosion resistance of stainless steel [17, 18–26]

The data reported about the role of Nb and cold deformation on the electrochemical behavior of stainless steel are very scarce.

In this work, the corrosion behavior of the austenitic stainless steel containing different amounts of niobium will be studied. The susceptibility of cold deformed niobium containing stainless steel to localized corrosion in 3.5% NaCl solution will be also investigated.

2. EXPERIMENTAL PART

2.1. Materials

The austenitic stainless steels ingots have been melted using a 40Kg vacuum induction furnace with different Nb contents and cast in permanent metallic mold. The chemical composition of steel alloys under investigation is shown in Table I.

Table I Chemical composition of austenitic stainless steel ingots

Ingot No.	C	Si	Mn	N	P	S	Cr	Ni	Mo	Nb	Ti
0	0.026	0.34	1.49	0.000198	0.038	0.007	18.20	9.78	0.22	0.003	0.027
1	0.024	0.38	1.44	0.000186	0.040	0.010	18.10	10.41	0.22	1.11	0.032
2	0.043	0.37	1.03	0.000021	0.042	0.013	17.70	9.98	0.21	1.14	0.031
3	0.0175	0.40	0.28	0.000132	0.041	0.0087	17.57	9.71	0.22	1.24	0.029

The ingots were hot deformed to different amount in the temperature rang 1200−750°C. Solution treatment was carried out at 1050°C for 1 h then rapid water quenching.

2.2. Surface Preparation

Series of specimens were abraded to 800 finishes with SiC grit papers, degreased in acetone, washed with distilled water, and dried in dry air.

2.3. Methods

2.3.1. Electrochemical impedance tests.

The corrosion behaviour of the previous specimens were monitored using electrochemical impedance spectroscopy (EIS) and DC polarization techniques during immersion in 3.5% NaCl solution open to air and at room temperature for up to 14 days.

A three-electrode set-up described elsewhere [27] was used with impedance spectra being recorded at the corrosion potential E_{Corr}. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Pt wire to reduce the phase shift at high frequencies. EIS was performed between 0.01 Hz - 65 kHz frequency range using a frequency response analyzer (Autolab PGSTAT 30, Eco-Chemie, The Netherlands). The amplitude of the sinusoidal voltage signal was 10 mV.

2.3.2. Polarization tests.

DC polarization tests of specimens previously immersed for two weeks in 3.5% NaCl solution were made at a scan rate of 0.07 mV/sec in the applied potential range from -0.15 V_{SCE} to 0.7 V_{SCE} with respect to E_{Corr} using an Autolab PGSTAT 30 galvanostat/ potentiostat, The Netherlands. The exposed surface area was 2.54 cm^2. All curves were normalized to 1cm^2.

2.3.3. Energy-dispersive spectrometry.

SEM images were obtained using a digital scanning electron microscope Model JEOL JSM 5410, Oxford Instruments, Japan, was used to examine the degree of corrosion products after immersion. Microprobe analysis was performed using energy dispersive spectrometry, EDS, Model 6587, Pentafet Link, Oxford microanalysis group, UK.

2.3.4. Surface morphology.

Corrosion morphology was examined with a metallographic microscope (LEICA DMR) with a Quips Programming window, LEICA Imaging Systems Ltd., Cambridge, UK.

3. RESULTS AND DISCUSSION

3.1. Effect of Niobium content

The impedance measurement technique has been applied to the study of pitting corrosion and other localized corrosion [27-31]. The impedance technique has marked advantages in the study of interfacial reactions and other interfacial phenomena. The impedance information obtained has time-resolved and surface-averaged characteristics [31].

In this work, the corrosion behavior of austenitic stainless steel specimens containing different amount of Nb alloying element was investigated using electrochemical impedance spectroscopy (EIS) in 3.5% NaCl. Nyquist plot (Fig. 1a) showed that the corrosion resistance increased by increasing the Nb contents. The surface resistance of austenitic stainless steel without Nb is $1.5X10^{4}$ Ωcm^{2}. The resistance slightly increased after addition of 1.1% Nb. Another increase was observed for the alloy containing 1.14% Nb to reach $2.2X10^{4}$ Ωcm^{2}.

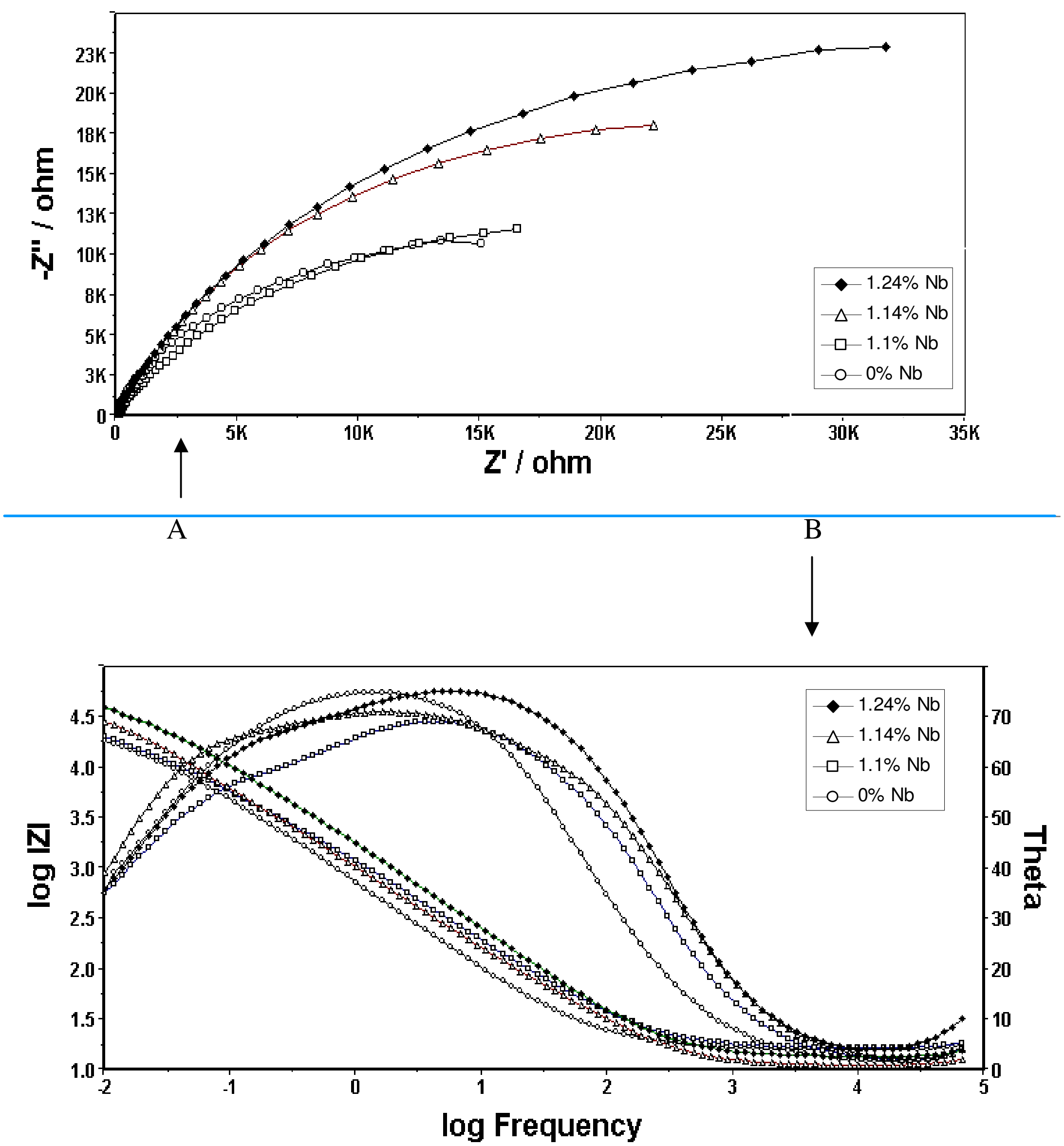


Figure1 (A) Nyquist and (B) Bode plots of austenitic stainless steel specimens with different Nb content after two weeks of immersion in 3.5% NaCl

The highest surface resistance was observed for 1.24% Nb alloy. A resistance of $3.4X10^4$ Ωcm^2 was recorded after 15 days of immersion in 3.5% NaCl. Bode plot showed that the pitting resistance of the austenitic stainless steels was generally improved by increasing the niobium content which was confirmed by the relaxation of the impedance spectra (Fig. 1b). This may be attributed to formation of Nb-rich oxide film.

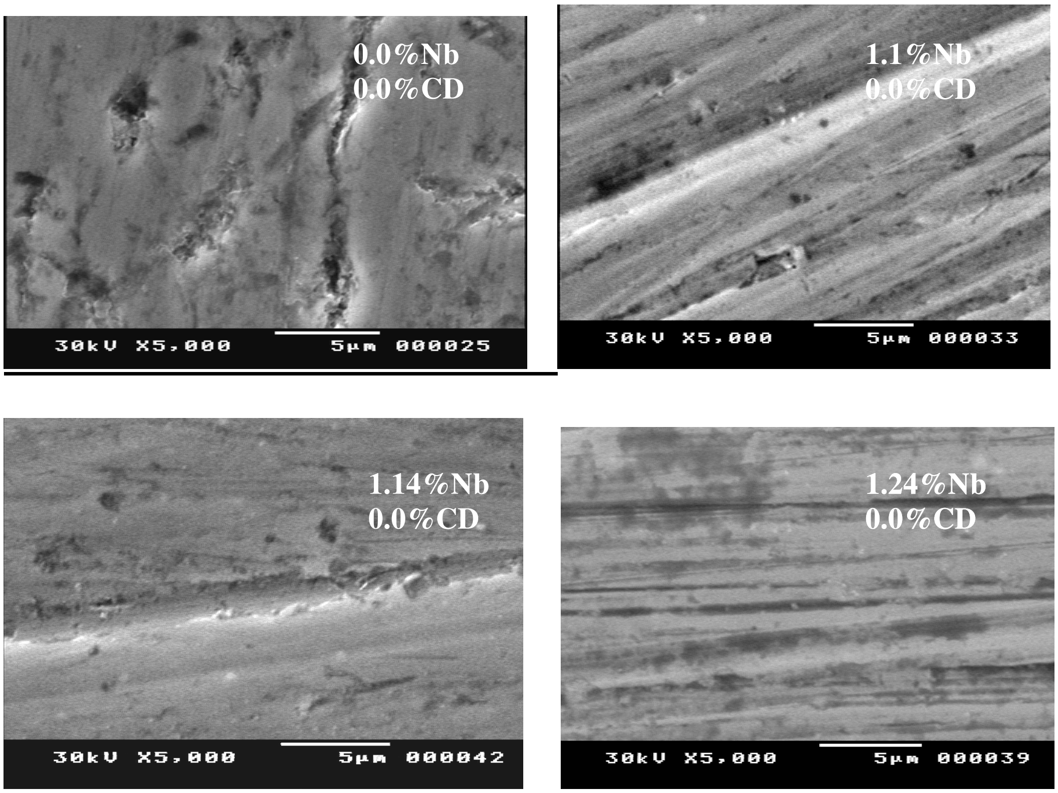


Figure 2: SEM of specimens with different Nb content before corrosion

SEM of the specimens containing different Nb ratios showed that the surface distribution improved by increasing the Nb content. The best oxide layer distribution was observed for specimen containing 1.24% Nb (Fig, 2). The amount of surface defects decreases by increasing the amount of Nb in stainless steel. Accordingly, the corrosion behavior of these alloys was expected where the severe intergranular corrosion was observed for 0% Nb alloy. Stainless steel alloy of 1.14% Nb showed microcraking oxide film. No pitting corrosion was observed for stainless steel containing 1.24% Nb after two weeks of immersion in NaCl (Fig. 3). However, microscopic examination showed few areas of crevice corrosion.

According to EIS, microscopic examination and visual inspection, the stainless steel alloy containing 1.24% Nb showed the best corrosion protection performance among the alloys studied. Therefore, it was resonable to containue studying the corrosion behavior of such alloy under different amount of cold deformation.

Polarization curves confirmed this result where as-polished specimens did not show any passive perfect zone. Conversely, an onset passive zone amounted to 65 and 5 mV for the specimens of 1.1%

Nb and 1.14% Nb respectively, was observed (Table II). Although the specimens of 1.24% Nb did not show any perfect passivity domain, the passive current of such specimens is about 3 folds lower than the specimens containing 1.1% Nb and 1.14% Nb. These results confirm the important role of Nb to enhance formation of Nb rich protective oxide film shifts the current to more noble one and consequently, reducing the number of pits.

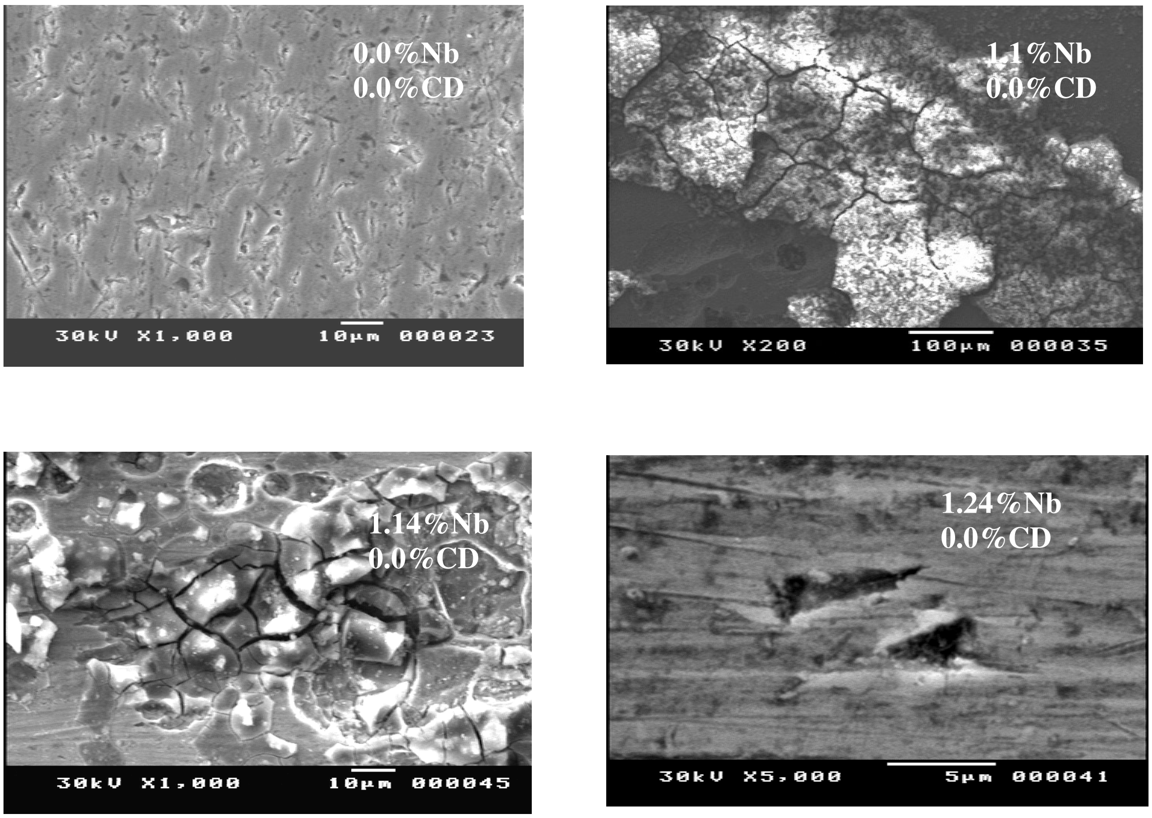


Figure 3: SEM of specimens with different Nb content after two weeks of immersion in 3.5 % NaCl

SEM and visual inspection confirmed these results where the number of pits was very small for the specimens containing 1.24% Nb compared with other specimens.

Table II Polarization data of after 15 days in NaCl

Specimen	Open circuit Potential(mV)	E_{pit} (mV)	Passive Current (A)	Perfect passivity Domain
0.0 % Nb	75	312	$1X10^{-7}$	Not present
1.10% Nb	340	152	$1X10^{-5}$	65 mV
1.14% Nb	323	172	$2X10^{-5}$	5 mV
1.24% Nb	37	294	$4X10^{-8}$	Not present

3.2. Effect of cold deformation

The influence of cold deformation on the corrsion resistance of 1.24 %Nb was studied. The electrical impedance spectroscopy measurments were performed for stainless steel alloy of 1.24% Nb content cold deformed at 0, 23, 40, 50%.

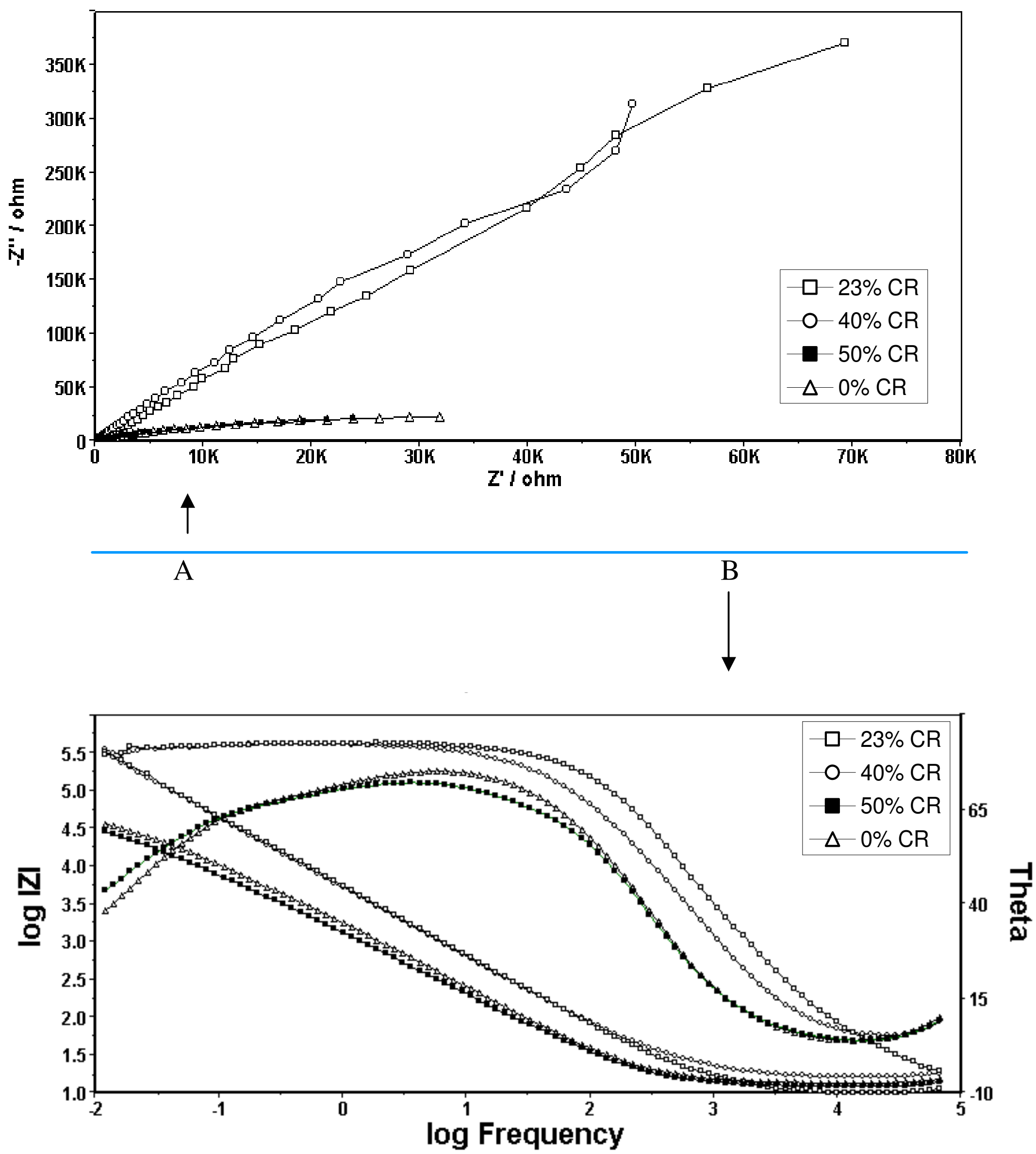
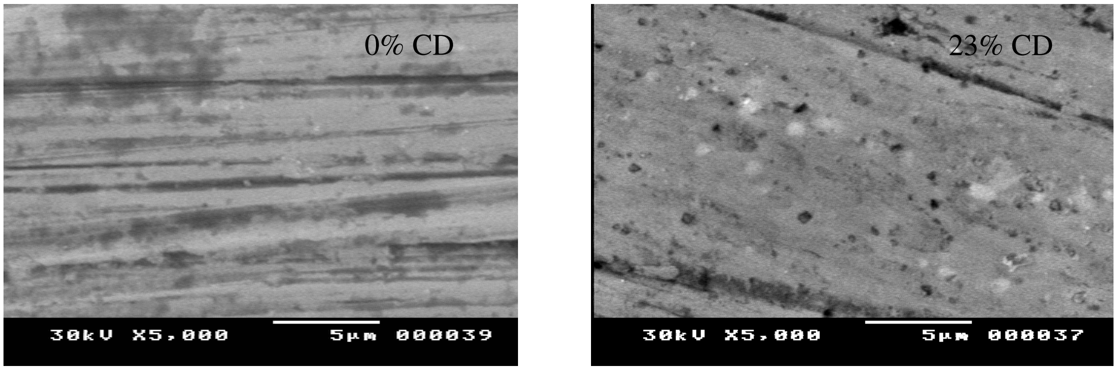
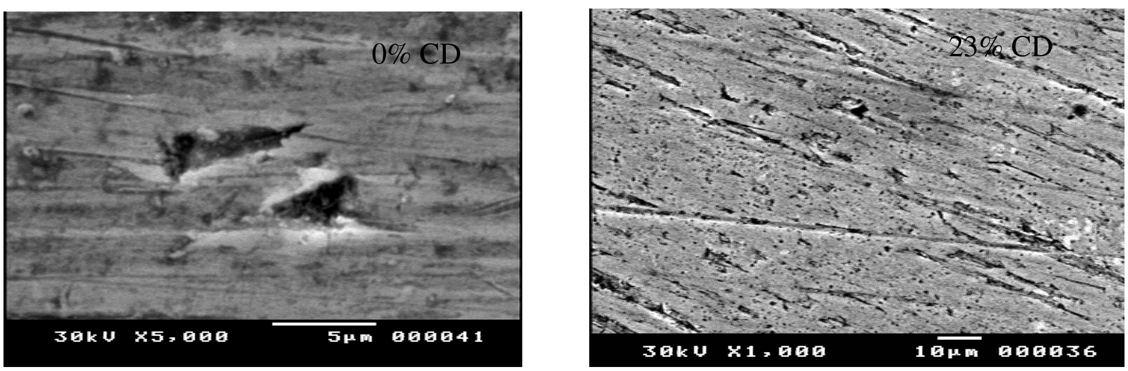


Figure 4: (A) Nyquist and (B) Bode plots of austenitic stainless steel specimens containing 1.24%Nb after two weeks of immersion in 3.5% NaCl at different amounts of cold deformation



before corrosion



after corrosion

Figure 5: SEM of specimens containing 1.24%Nb with different amount of cold deformation

Nyquist and Bode plots (Figs 4 a and b) showed that cold deformation has a critical effect on corrosion resistance. By increasing the amount of cold deformation to 23% the corrosion resistance sharply improved and the surface resistance increased from $3.4X10^4$ Ωcm^2 to $7X10^4$ Ωcm^2 after two weeks of immersion in NaCl solution. SEM showed that the surface of 23% cold deformation specimen had a smooth apperance which suggest that the 23% deformation decreased the active anodic sites on the surface and hence decreased the chance of localized corrosion to occure. Increasing the amount of cold deformation up to 40% and 50% affect negatively the corrosion resistance. It seems that by increasing cold working >23%, strain induced martensite and residual stresses are significantly introduced on the surface, which affects the localized corrosion resistance by increasing the number of active anodic sites on the surface [32]. According to Bode plot (Fig. 4b) the sample deformed at 50% showed a dramatic decrease of the impedance in the capacitive region, which is characteristic for the pitting process on stainless steel. In addition, the phase angle θ tended toward zero at low frequencies, indicating that the resistance of the barrier layer was being approached. These changes of the spectra at very low frequencies indicated the occurrence of pitting and were in agreement with the visual and SEM inspection. On the other hand, the samples deformed at 23% showed very stable impedance behavior even after two weeks of immersion in NaCl solution, indicating that cold deformation has a critical effect on the corrosion resistance of stainless steel.

EDS analysis confirmed these results where the amount of Nb detected in the specimen cold deformed at 23% was higher than that detected for the specimens without deformation as shown in Table III. These results suggest that the higher corrosion resistance observed for 23% cold deformed specimen is mainly due to formation of Nb-rich oxide film disteributed uniformely over the surface (Figs 5a and b).

Table III Atomic ratio of Nb after two weeks in NaCl.

Alloy	Nb Atomic ratios
0% CR	0.49
23% CR	1.16

4. CONCLUSIONS

- EIS is a powerful technique to investigate the corrosion protection of stainless steel.
- Localized corrosion is a serious problem of stainless steels when they are exposed to chloride solutions.
- According to EIS measurements, increasing Nb content results in increasing the localized corrosion resistance of austenitic stainless steels in NaCl.
- Cold deformation (CD) has a critical rule on the corrosion resistance of stainless steel. The corrosion resistance increased by increasing CD up to 23%. Further increase in the amount of CD affects negatively localized corrosion resistance.
- The best localized corrosion resistance was obtained from the alloy containing 1.24% Nb and 23% cold deformation.

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