

Effect of Niobium in the Phase Transformation and Corrosion Resistance of One Austenitic-ferritic Stainless Steel

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Austenitic-ferritic stainless steels containing 0.2% and 0.5% niobium were evaluated with respect to the microstructures, microhardness, pitting potential resistance, electrochemical impedance and wearing tests. Niobium is an alphagenic element and has a great influence on phase transformation of duplex stainless steels. In the present investigation, the samples were annealed at 1050 °C and aged at 850 °C to promote the formation of sigma phase. The pitting potential resistance and electrochemical impedance were evaluated in 3.5 % sodium chloride solution. The wear coefficients were calculated by micro-wear tests conducted using a fixed ball machine and aluminum oxide as abrasive. The results show that the niobium content lead to increase on Laves phase formation. This phase, in association with the sigma phase, causes a significant increase in the hardness and wear resistance with a decrease on corrosion resistance of the austenitic-ferritic stainless steels.

Keywords: duplex stainless steel containing niobium, sigma phase, Laves phase, wear coefficient, pitting potential, charge transfer resistance

1. Introduction

In austenitic-ferritic or duplex stainless steels, the microstructure is basically determined by the chromium and nickel contents, which act as stabilizers of the ferritic or austenitic phases. Currently, austenitic-ferritic stainless steels are being used in replacement of austenitic stainless steels in industrial applications, where requirements for corrosion resistance and mechanical strength are greater¹.

Equipment like pressure vessels, reactors and storage tanks for use at high temperatures or in aqueous environments with chlorides, are manufactured with austenitic-ferritic stainless steels. In the oil industry, these steels are used in the manufacturing of pumps that inject saltwater to expel gas and oil^{2,3}.

The microstructure constituted by elongated austenitic grains with alternate regions of ferrite and intermetallic phases depends on their chemical composition and heat treatment. Another important factor is that in austenitic-ferritic steels, the nitrogen replaces partially nickel, with improvement in mechanical properties and cost reduction⁴.

In these steels, solidification starts at about 1450 °C with the formation of ferrite (α), which gives origin to austenite (γ) near 1300 °C⁵. The σ phase nucleates preferentially in interface α/γ incoherent with the matrix in the range of 600 to 950 °C and compromises the cast steels toughness^{6,7}.

This phase has a tetragonal crystalline structure with 900 to 1000 hardness Vickers, it is not magnetic at room temperature and is composed of iron, chromium and molybdenum^{8,9}.

In aggressive environments, the preferential attack promotes the reduction of chromium and molybdenum near

the sigma phase particles. That is one of the most common explanations for the reduction on pitting corrosion resistance in these steels¹⁰. Sigma phase reduces the elongation and toughness too, although it increases hardness, yield point and tensile strength in the matrix. Precipitation of 1% of this phase reduces by 50% the initial value of the absorbed energy in the Charpy test^{11,12}.

According to the literature, niobium has a great influence on phases transformation of austenitic-ferritic stainless steels, besides promoting grain refinement in the microstructure^{13,14}.

Considering the interest to develop materials for use in the petrochemical industry, the proposal of this study was to evaluate the niobium effect on microstructure, hardness and phase transformation in the SEW 410 Nr.14517 austenitic-ferritic stainless steel. The pitting potential resistance, charge transfer resistance and wear resistance were determined too, after annealed and aged. Heating treatment at 850 °C was performed to promote sigma phase formation in these steels¹⁵.

2. Experimental Procedures

The SEW 410 Nr. 14517 and SEW 410 Nr. 14517 alloys modified with 0.2 and 0.5% were elaborated in an electric induction furnace with a system for vacuum degasification with capacity of 1000 kg. The liquid metal was poured out in sand molds agglomerated with urethane phenolic resin and the cast blocks were annealed at 1050 °C for one hour. Two samples were cut and analyzed in an optical emission spectrometer. After, samples in the form of discs with diameter 12 × thickness 8mm were cut and heated at 850 °C for 15, 30 and 60 minutes. The cooling was done in air.

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Afterward the samples were prepared according to conventional metallographic methods. In order to quantify the percentage of phases they were immersed in Behara reagent (125 ml water, 25 ml hydrochloric acid, 3g ammonium bifluoride and 0.2 g potassium metabisulfide). Thus they were observed by optical microscope and Electron Backscatter Diffraction technique (EBS) on Scanning Electron Microscope (MEV). During observations, the Energy Dispersive X-ray Spectroscopy technique (EDS) was used to determine the chemical compositions of sigma and Laves phases.

The amounts of austenitic phases (twenty regions in one sample) were determined by optical microscopy, magnetic ferritic phase with use of ferritoscope FMP-30 (Helmut Fischer) and sigma phase by Equation 1. The results obtained by ferritoscope analyzes, as the A800/A800M-91(1997) standard, represent the average of ten measurements for each sample.

$$\% \text{ Sigma Phase} = 100 - (\% \text{ austenitic phase} + \% \text{ ferritic phase}) \quad (1)$$

The microstructural effects on the steels were evaluated by microhardness measurements on the samples, before and after heat treatment. The averages of five measurements were obtained with load of 100 g using a Vickers hardness tester.

In order to compare the corrosion resistance of the steels, the pitting potential resistance and electrochemical impedance spectroscopy curves were obtained in 3.5 % sodium chloride electrolyte. In the setting up of electrochemical cell, austenitic-ferritic stainless steel was used as work electrode, saturated calomel as reference electrode and platinum as auxiliary electrode. The experiments were carried out by anodic polarization technique with a scan rate of 1.0 mV/s, from 700 mV cathodic until 1.5V at room temperature (25 °C). In order to establish the open circuit potential (OCP), prior to measurements, the samples were immersed in solution for about 30 min. The electrochemical impedance measurements were taken after a steady state with amplitude of 10 mV AC and in the range of 100 KHz until 0.1 mHz. The results represent the average of five measurements for each sample.

To evaluate the wear resistance on the surface of steels, the wear coefficients were calculated by tests using a fixed ball machine and aluminum oxide as abrasive. Spheres with diameter 25.4 mm and rotational speed of 350 rpm were used. For abrasive condition, the applied load was 13 g (0.13 N). Consecutive wear scars were performed, only on a sample for each condition, with test times of 3, 6, 12 and 18 min¹⁶.

3. Results

Table 1 gives the chemical compositions of the austenitic-ferritic steels SEW 410 Nr. 14517 elaborated for this study. EDS chemical analysis presented 56Fe33Cr5Ni4Mo2Cu in sigma phase and 39Cr28Fe26Nb3Mo2Ni2Cu in the Laves phase (Figures 5 and 6).

Figures 1 to 6 illustrate the microstructural characteristics of the austenitic-ferritic stainless steel, with and without niobium, after heat treatments.

Figures 7 and 8 represent the charge transfer resistances against hardness and niobium contents on stainless steels.



Figure 1. Steel without niobium: annealed sample shows elongated austenite grains in ferritic matrix. BSE after Behara etching.

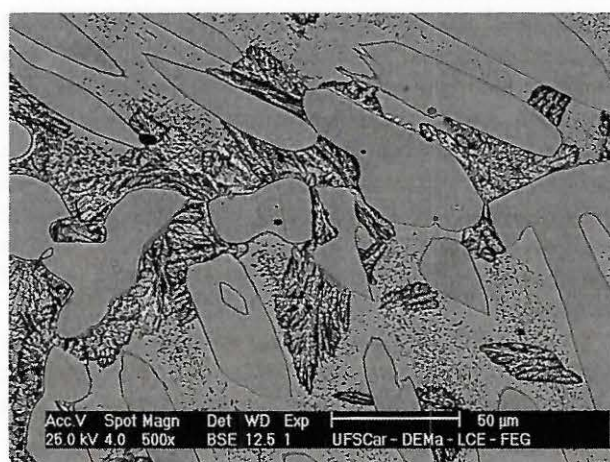


Figure 2. Steel without niobium: it can be observed the beginning of sigma transformation, after annealed and aged at 850 °C/15minutes. BSE after Behara etching.

Table 1. Chemical compositions of standard and austenitic-ferritic stainless steel SEW 410 Nr. 14517 with and without niobium (% in weight).

	C _{max}	Cr	Ni	Mo	Cu	Mn _{max}	Si _{max}	N	P _{max}	S _{max}	Nb
SEW 410	0.03	24.0	5.0	2.5	2.8	2.0	1.0	0.12	0.03	0.02	-
Standard		26.5	7.0	3.5	3.5			0.25			
SEW 0.0Nb	0.03	26.0	6.4	3.2	3.0	1.5	0.8	0.22	0.03	0.01	-
SEW 0.2Nb	0.03	26.0	6.5	3.2	2.9	1.3	0.7	0.21	0.03	0.01	0.2
SEW 0.5Nb	0.03	26.0	6.3	3.2	3.0	1.4	0.8	0.21	0.03	0.01	0.5

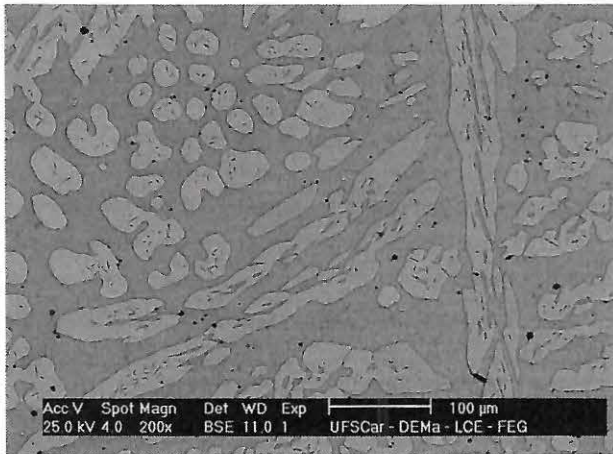


Figure 3. Steel modified with 0.2% niobium: annealed sample shows elongated austenite grains in ferritic matrix. BSE after Behara etching.

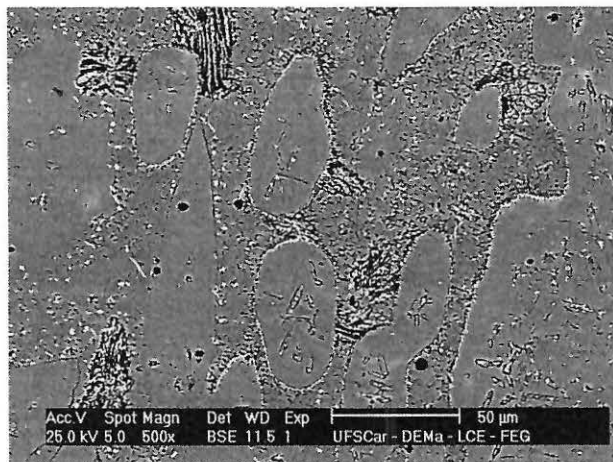


Figure 4. Steel modified with 0.2% niobium: there is a smaller amount of sigma phase than steel without niobium after annealed and aged at 850 °C/15 minutes. There is not Laves phase. BSE after Behara etching.

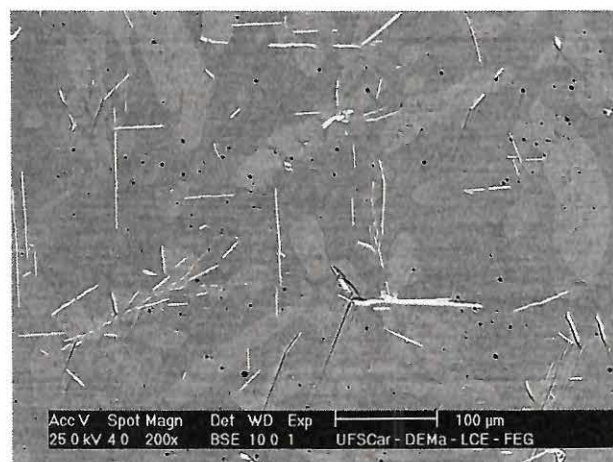


Figure 5. Steel modified with 0.5% niobium: Laves phase appears as needles after annealed. BSE after Behara etching.



Figure 6. Steel modified with 0.5% niobium: annealed and aged for one hour at 850 °C. Laves phase appears as needles associated with sigma phase. BSE after Behara etching.

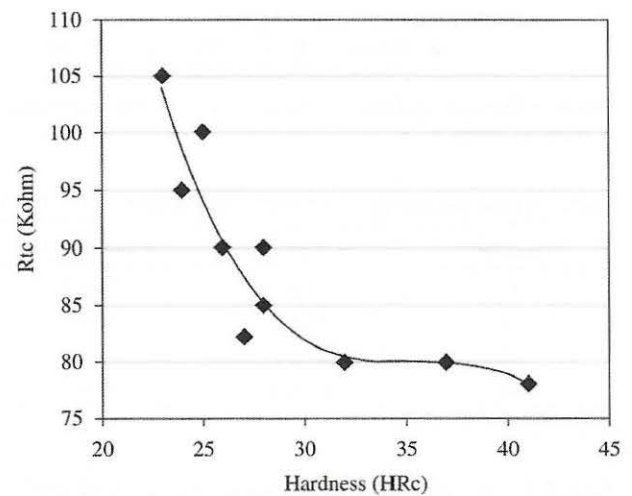


Figure 7. Charge transfer resistance for the steels regarding the hardness.

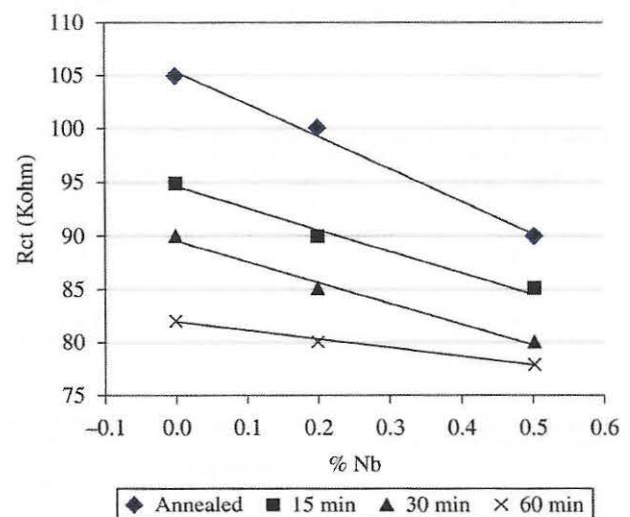


Figure 8. Charge transfer resistance for the steels regarding the niobium containing.

Figure 9 illustrates the wear coefficients values against aged times and niobium contents on austenitic-ferritic stainless steels.

Table 2 lists the percentage of phases and microhardness values of the SEW 410 Nr.14517 without niobium, after heat treatments. Annealed sample represents the value for zero minutes at 850 °C.

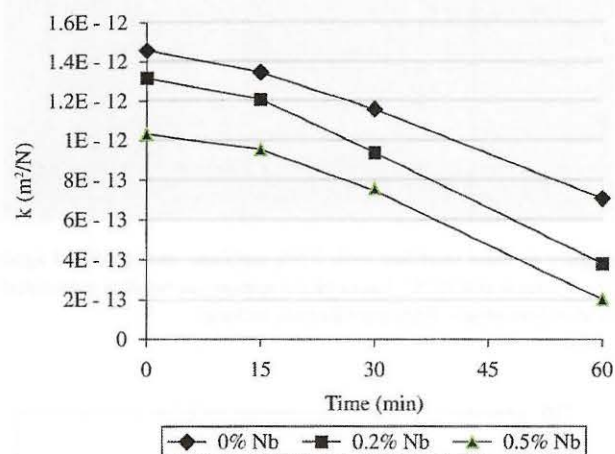


Figure 9. Effects of niobium and heating time on wear coefficients of stainless steels.

Table 2. Phases percentage and Vickers microhardness of stainless steel without Nb.

Time (min)	Ferrite (%)	Austenite (%)	Sigma (%)	Ferrite+σ (HV)	Austenite (HV)
0 ^[a]	46 ± 2	54 ± 2	0,00	290 ± 10	255 ± 08
15	23 ± 2	52 ± 2	25 ± 2	520 ± 20	264 ± 12
30	09 ± 1	51 ± 2	40 ± 2	563 ± 15	263 ± 07
60	1 ± 0.1	53 ± 3	46 ± 3	650 ± 12	258 ± 10

^[a]annealed sample.

Table 3. Phases percentage and Vickers microhardness of stainless steel containing 0.2% Nb.

Time (min)	Ferrite (%)	Austenite (%)	Sigma (%)	Ferrite+σ (HV)	Austenite (HV)
0 ^[a]	45 ± 2	55 ± 3	0.00	305 ± 10	260 ± 03
15	32 ± 2	53 ± 3	15 ± 3	340 ± 20	262 ± 05
30	16 ± 3	55 ± 4	29 ± 4	576 ± 15	283 ± 04
60	07 ± 1	52 ± 4	41 ± 4	692 ± 12	292 ± 03

^[a]annealed sample.

Table 4. Phases percentage and Vickers microhardness of stainless steel containing 0.5%Nb.

Time (min)	Ferrite (%)	Austenite (%)	Sigma (%)	Ferrite+σ (HV)	Austenite (HV)
0 ^[a]	47± 2	52 ± 2	0,00	314 ± 15	263 ± 05
15	29 ± 1	53 ± 3	18 ± 3	450 ± 20	276 ± 06
30	05 ± 1	52 ± 3	43 ± 5	576 ± 15	290 ± 04
60	1 ± 0.1	54 ± 5	45 ± 5	609 ± 12	292 ± 04

^[a]annealed sample.

Table 5. Pitting potentials of stainless steels after annealed and aging at 850 °C.

	Annealed	15 min	30 min	60 min
SEW 0.0 Nb	1.23 ± 0.11V	1.16 ± 0.03V	1.11 ± 0.01V	1.09 ± 0.01V
SEW 0.2 Nb	1.15 ± 0.03V	1.07 ± 0.03V	1.03 ± 0.01V	1.01 ± 0.01V
SEW 0.5 Nb	0.90 ± 0.03V	0.77 ± 0.03V	0.66 ± 0.01V	0.60 ± 0.02V

Tables 3 and 4 list the percentages of phases and microhardness values of the SEW 410 Nr.14517 with 0.2 and 0.5% Nb, after heat treatments.

Table 5 lists the pitting potentials values of the of the SEW 410 Nr.14517 stainless steel without niobium and modified with 0.2 and 0.5% Nb, after heat treatments.

Table 6 lists the charge transfer resistance values of the austenitic-ferritic stainless steels after heat treatments.

4. Discussion

The chemical compositions shown in Table 1 reveal that the steels are according to SEW 410 Nr.14517 standard. Figures 1 to 6 represent the microstructural characteristics of austenitic-ferritic stainless steels without and containing 0.2 and 0.5% niobium, after heat treatments. The higher content of niobium promotes the Laves phase formation, as can be seen in the last one (Figures 5 and 6)¹⁷.

In relation to Figures 1, 3 and 5, annealed samples, there is a distribution of elongated austenite white grains surrounded by black ferritic matrix. According to the literature, the amounts of austenitic and ferritic phases are related to the content of alloying elements and annealing temperature. Regarding the austenitic phase, there was no significant variation in values determined by optical microscopy.

Table 6. Charge transfer resistances of steels after annealed and aging at 850 °C.

	Annealed (kΩ/cm ²)	15 min (kΩ/cm ²)	30 min (kΩ/cm ²)	60 min (kΩ/cm ²)
SEW 0.0 Nb	105 ± 1	95 ± 1	90 ± 2	80 ± 2
SEW 0.2 Nb	100 ± 2	90 ± 2	85 ± 2	80 ± 2
SEW 0.5 Nb	90 ± 2	85 ± 2	80 ± 2	78 ± 2

In the stainless steel containing 0.2 niobium after heating for 15 minutes at 850 °C, it is possible to observe the austenitic surrounded by ferritic plus sigma phase (Figure 4). Sigma phase nucleates preferentially in interface α/γ incoherent with the matrix and grows at the expense of the ferritic phase (Figure 2). It can be noted more sigma phase in the stainless steel without niobium. In steels containing niobium and without niobium the sigma amount increases with the time.

There is a tendency of the ferritic matrix becomes into eutectoid austenite more sigma, which is almost complete after 60 minutes at 850 °C¹⁰¹. In relation to sigma phase, the EDS chemical analysis presented 56Fe33Cr5Ni4Mo2Cu. Sigma phase may precipitate in the interface and inside the austenitic grain. It is likely, that the transformation occurs due to the increase on number of vacancies and heating time^{18,19}.

The transformation occurs with reduction of chromium and molybdenum in regions near sigma phase. It is mainly responsible for increases the corrosion speed by eight times in austenitic-ferritic stainless steels^{6,10}.

With regard to Tables 2, 3 and 4, the values confirm that after heating at 850 °C, the amount of ferrite is higher in the steel containing 0.2% niobium. In relation to the niobium content, the alphagenic effect is mostly observed in this steel.

In the steel containing 0.5% niobium there is a precipitation of Laves phase, constituted mainly of iron, niobium and chromium. Laves phase precipitates as needles and it is associated with weakening of the steel¹⁴. Annealed at 1050 °C is unable to solubilize this phase. EDS chemical analysis presented 39Cr28Fe26Nb3Mo2Ni2Cu in the needles.

Laves phase impairs the niobium alphagenic effect in this steel. It is possible that the chrome reduction around the Laves phase destabilizes the ferritic matrix and favors the $\alpha \rightarrow \sigma$ transformation. This explains the higher quantity of sigma in the steel containing 0.5% Nb with respect to containing 0.2% Nb after heating at 850 °C. Laves phase provokes the reduction of chromium in matrix and reduces the pitting corrosion resistance.

With respect to the hardness, the austenitic phase measurements were easily obtained in a Vickers hardness tester, unlike sigma. In this case, the measurements were obtained from regions with ferritic phase associated with sigma²⁰. Tables 2, 3 and 4 show the hardness measurements. Laves and sigma phases, associated with the niobium dissolved in matrix, increase the hardness of these steels. The niobium effect in hardness can be proven in the Figure 9, because the wear coefficient reduces in the annealed stainless steels, when the element increases. In this case, there is Laves phase only in the steel containing 0.5% niobium.

As can be seen from Table 5 pitting potential values decrease when volumetric percentage of sigma and niobium increase²⁰. Sigma phase is rich in chromium and occurs preferentially at the interface α/γ with the depletion of this element in the ferritic phase. It is one of the most common explanations to reduce the pitting corrosion resistance^{9,14}. However, these steels have similar pitting corrosion resistance to the austenitic stainless steel in annealed conditions¹⁹.

According to the charge transfer resistance in chloride environment, the values in Table 6 decrease when sigma phase increases. Sigma phase removes the chromium of the ferritic matrix and reduces the corrosion resistance. It can be noted that Laves phase contributes to reduce the corrosion resistance in the steel containing 0.5% Nb too.

Figure 7 shows the decrease in the charge transfer resistance, due to the sigma and Laves phase that lead an increase on hardness of these steels. Considering the same niobium content, the charge transfer resistance reduces when the heating time increases (Figure 8).

From the wear resistance, it can be seen in Figure 9 that the wear coefficients values reduce when niobium increases. Niobium in solution and sigma associated with Laves phase, promote an increase on hardness and wear resistance of these steels.

Finally, the results show a negative contribution to the corrosion resistance with niobium increasing, although the hardness of the sigma phase can favor the use of these steels in slightly aggressive environments, where the wear resistance is a factor to be minimized.

5. Conclusions

The results of this research show that:

- niobium presents an alphagenic effect after heat treatments at 850 °C mainly in the steel containing 0.2% Nb;
- pitting potential and charge transfer resistance reduce when the niobium increases;
- corrosion resistance reduces when the heating time at 850 °C increases;
- sigma and Laves phases reduce the pitting corrosion resistance;
- sigma and Laves phases leads to an increase on hardness and wear resistance;
- Laves phase appears with the addition of 0.5% niobium and is insoluble at 1050 °C;

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