

# Corrosion of Stainless Steels with “Soft” Martensitic Structure

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*One of the most efficient methods for prevention or slowing down the corrosion is the improved selection of chemical resistance of the employed material and the optimization of the microstructure by adequate heat treatments. The present work is concerned with characterizing the corrosion resistance of four martensitic stainless steels, cast by SC UCM Reșița after genuine recipe and having a content of (13...17)% chromium and (0...4)% nickel. Before the corrosion tests the specimens were subjected to a heat treatment consisting in a body martensitic quenching from the austenitic domain (980...1090°C), followed by tempering at approximately 600°C. The tests were carried out in acetic acid and synthetic seawater both at room and boiling temperature.*

*Keywords: corrosion, environment, chemical composition, stainless steel, microstructure, heat treatment*

The deterioration of materials under the environment influence is generally called corrosion. The metals are obtained from ore by the reduction semi-reaction of the global redox reaction. When used, the metal enters a semi-reaction oxidation with the working environment, the complementary part of redox. For the users, this situation is undesirable as a result of the running characteristics worsening [2, 3, 4, 7].

The financial losses determined by this kind of degradation are considerable. Statistical data [8] show that, in the developed countries, the direct and indirect costs determined by corrosion are estimated to reach 4% of the gross national product. The National Institute of Standards and Technology estimates that corrosion annually costs the United States \$70 billion, of which at least \$10 billion could be prevented by a good selection of materials [9].

With few exceptions, the corrosion resistance of metals is considered as a surface property. The elements that influence this resistance are bounded both to the material and environment. The possibility to influence the environment is very reduced because it is determined by the specific service process.

For steels, among the elements that favour the corrosion, the heterogeneousness of the structure and the chemical composition (sulphides, oxides, carbides, nitrides etc.) must be considered. All these elements can form an electrochemical cell. The presence of grains having different potential or crystallographic orientations can also induce chemical attacks. The grain boundaries are zones

with increased vulnerability as the result of impurities segregation. Investigations regarding hardening indicate, that in some cases, the difference appearing between the zones affected by **cold hardening** and those unaffected by **cold hardening** can cause, at their turn, chemical attack [8]. Therefore, among the methods for solving the corrosion problem, the correct selection of the chemical composition and the optimization of the structure through adequate heat treatments are the most efficient procedures.

With respect to the environment, the main reasons that accentuate the corrosion are:

1. the existence of oxidizing elements;
2. the increase of the dissolved oxygen content (even in a stream of water the corrosion is more aggressive than in stagnant water);
3. the increase of temperature.

The present work is concerned with the corrosion resistance of martensitic stainless steels having (13...17)% chromium and (0...4)% nickel, tested in two different aggressive environments (acetic acid and synthetic seawater). Out of the eight basic forms of corrosion there were investigated only two, the uniform and the intergranular corrosion.

*Chemical composition and heat treatment of the tested steels*

The “soft” martensitic steels are iron-chromium alloys with a content of (13...17)% chromium and (0.04...0.08)%

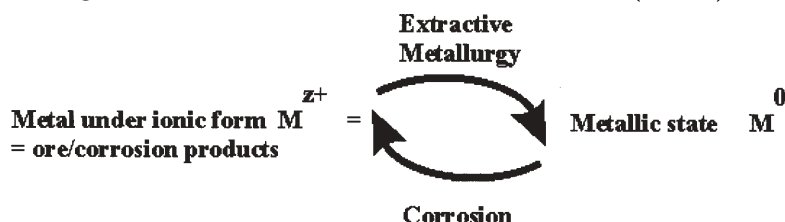


Fig. 1. Comparison between corrosion and extractive metallurgy

**Table 1**  
CHEMICAL COMPOSITION OF THE TESTED STEELS

Steel	Chemical elements %										
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	Fe
13 Cr	0,078	0,23	0,67	0,02	0,021	13,1	-	0,10	0,025	0,13	Rest
13 Cr-4 Ni	0,064	0,28	0,61	0,019	0,022	13,2	4,1	0,12	-	0,11	Rest
13 Cr-6 Ni	0,059	0,31	0,63	0,021	0,022	13,08	6,06	0,18	0,05	-	Rest
17 Cr-4 Ni	0,067	0,29	0,66	0,019	0,021	17,18	4,27	0,14	0,07	0,12	rest

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**Table 2**  
CORROSION RATE IN ACETIC ACID

Steel	Penetration index <mm/year>		
	5% CH <sub>3</sub> COOH, t =+25 <sup>0</sup> C	10% CH <sub>3</sub> COOH, t =+25 <sup>0</sup> C	10% CH <sub>3</sub> COOH, at boiling
13 Cr	0,138	1,048	14,281
13 Cr-4 Ni	0,047	0,075	10,055
13 Cr-6 Ni	0,031	0,055	9,329
17 Cr-4 Ni	0,013	0,046	7,993

**Table 3**  
CORROSION RATE IN SYNTHETIC SEAWATER

Steel	Penetration index <mm/year>	
	t=+22 <sup>0</sup> C	t=+100 <sup>0</sup> C
13 Cr	0,021	0,359
13 Cr-4 Ni	0,014	0,289
13 Cr-6 Ni	0,011	0,269
17 Cr-4 Ni	0,007	0,204

carbon [4, 5, 6]. The most important condition for a good corrosion resistance is to dissolve the entire chromium content in the solid solution. In this case, a dense and compact protective pellicle of chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) is formed on the surface. If there are carbide precipitations, the chromium content of the solid solutions diminishes and the protective layer receives a biphasic structure that reduces the corrosion resistance [7, 11]. When a part of the chromium content is bounded with the carbon, in form of Cr<sub>23</sub>C<sub>6</sub> carbides, the rest of the chromium content in the solid solution can be estimated with the relation:

$$\%Cr_{\text{dissolved}} = \%Cr - 14.54\%C \quad (3)$$

For improving the corrosion resistance, in neutral or weak oxidant environments, nickel can be added [1], but the cost price is raised. In the same time, nickel improves some mechanical characteristics such as tenacity and ductility because it reduces the content of the delta ferrite in the microstructure and retains some austenite, even at room temperature. In Table 1 the chemical composition of tested steels manufactured at SC UCM Resita SA is presented.

For a good corrosion resistance, the minimum chromium content of the tested steel is 12%. At this content of chromium, the mean carbon content must be restricted at 0.08% in order to prevent carbides precipitations near the grain boundaries.

Another factor that influences the stainless steels microstructure is the applied heat treatment. In our case the steels were subjected to a heat treatment consisting in a body martensitic quenching, from the austenitic domain (980...1090°C), followed by a tempering at approximately 600°C. Although the mechanical properties obtain high values [10, 11], sometimes the corrosion resistance remains insufficient.

### Uniform corrosion

The corrosion tests were carried out in two aqueous solutions, namely acetic acid (in conformity with the international standards [6, 7]) and synthetic seawater [12], both at room and boiling temperature. The cast specimens were heat treated and afterwards rough machined and finished. The corrosion losses, in mass unities, were measured and afterwards they were divided with the area of tested surface, the exposure time and the specific mass. For each trial type, (environment, temperature) there were used nine specimens and the exposure duration was 12 days.

The erosion rate, for each specimen, was computed every day. Later on, the corrosion rate per year was also estimated (with the hypothesis that the corrosion is constant) expressed as the penetration index (mm/year). The results are presented in tables 2 and 3. Analyzing the data, we obtained the conclusion presented below.

When the heat treatment assures a great quantity of chromium dissolved in the solid solution, the erosion rate is diminished with the increase of the specified chemical element (compare 13Cr-4Ni with 17Cr-4Ni).

The increase of the nickel content till 6% determines the raise of the corrosion resistance (compare 13 Cr with 13Cr-4Ni and 13Cr-6Ni). It results that an optimum rate Cr/Ni increases the resistance to corrosion.

By increasing the concentration or the temperature of the aqueous solution, the corrosion losses are also greater.

### Intergranular corrosion

This type of corrosion is especially common in austenitic stainless steels and manifests itself in the form of localized points along the grain boundaries with only slight attack of the grain faces.

In order to put into evidence the intergranular corrosion the specimens were attacked with the following solution: 160 g of copper sulfate, 100 mL of distilled water and copper chips. The specimens were introduced in a bottle with ascendant refrigeration. For every cm<sup>3</sup> of specimen volume (20mmx20mmx5mm) there were used 20 mL of solution. The boiling continued for 24 h, assuring permanently the cooling of the refrigerant. Finally the specimens were subjected to bending at 90°.

The macrographic images were obtained with a stereomicroscope and are presented in figure 2. The area subjected to tensile stresses is presented in figure 2a and that subjected to compression in figure 2b.

The microstructure of the same specimens examined with an electron-scanning microscope (fig. 3), shows that the investigated steels are not sensitive to intergranular corrosion.

As a result of the low carbon content, the carbides precipitations are not so intense as in conventional martensitic stainless steels. When the steels are heated with the view of quenching, the carbon is dissolved in the austenite and this condition suffers insignificant modifications when the martensitic transformation occurs.

The presence of nickel, as alloy element, reduces the proportion of delta ferrite, a structural constituent that worsens all mechanical characteristics. The tempering

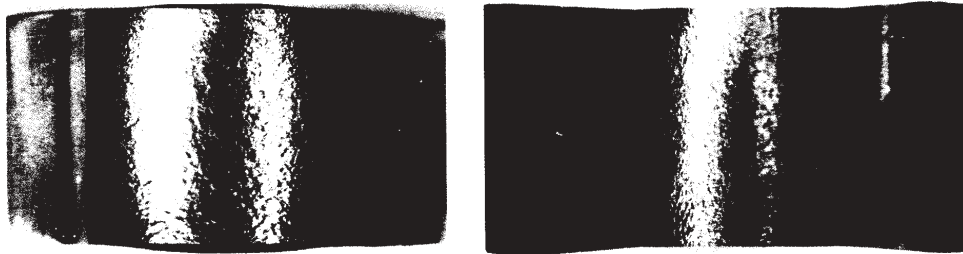


Fig. 2. Macrographic aspects of 13Cr-4Ni steel specimens tested to intergranular corrosion, after bending; a- area subjected to tensile stresses, b- area subjected to compression stresses

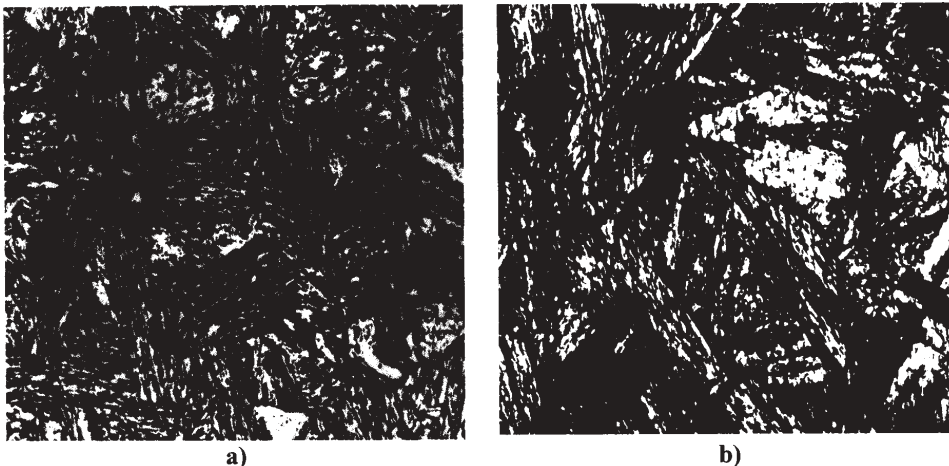


Fig. 3. Micrographic aspects of 13Cr-4Ni steel specimens tested to intergranular corrosion a - enlargement 1,000x; b - enlargement 5,000x

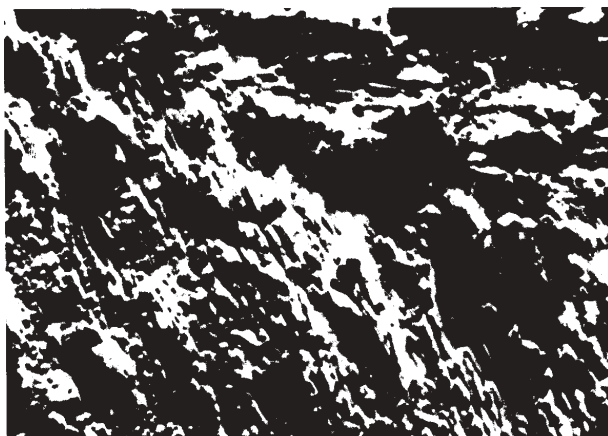


Fig. 4. Uniform disposition of fine carbides (enlargement 15,000x)

heat treatment promotes the precipitations in the form of extremely fine carbides. Most of these constituents appear inside the crystalline grain and not in its boundaries. The image in figure 4 obtained with an electron microscope at an enlargement of 15,000 confirms this allegation. Often these precipitations determine an impoverishment in chromium of the entire surface of the grains [2], and the starting of the corrosion will be extremely rare for these steels.

### Conclusions

The corrosion rate of “soft” martensitic stainless steels in aqueous solutions depends essentially both on the aggressive environment parameters (nature, concentration, temperature, etc.) and on the chromium content dissolved in the solid solution.

The presence of nickel in the chemical composition of these steels improves the corrosion resistance.

The microstructure obtained with the secondary heat treatment, consisting in air cooling from 980...1090°C

followed by a tempering at approximately 600°C, assures a maximum resistance against intergranular corrosion, as a result of the fact that the carbides precipitations take place inside the grains and not on their boundaries.

The stainless steels without content of nickel are not recommended for use in corrosive environments, because of their reduced resistances (the penetration index is between 0.1...1 mm/year, even in seawater at environmental temperatures).

The stainless steels with 13% Cr and 4...6% Ni can be used for pieces running in river or sea water (for ship propellers) because of their resistance at this type of corrosion (the penetration index is between 0.01...0.1 mm/year). The steel containing 17% Cr and 4% Ni is very resistant to corrosion in seawater (0.001...0.01 mm/year).

For chemical industry, these steels must be used with increased precautions, even at environment temperatures.

For such services, further investigations (regarding the compatibility with different environments) are needfull.

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