

STUDIES AND RESEARCH ON THE CORROSION BEHAVIOUR IN A 3.5% NaCl SOLUTION OF SINTERED 316 STAINLESS STEELS

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ABSTRACT

Products made from austenitic 316 stainless steels obtained through powder metallurgy technologies are used in many applications across various industrial fields due to their resistance to corrosion from air, water, and different acids. They are also non-magnetic, possess good mechanical properties at both low and high temperatures, offer good creep resistance, and have good weldability. This paper presents a series of experimental studies on the corrosion behaviour of sintered austenitic 316 stainless steels in a 3.5% NaCl solution. The different behaviours observed can be attributed to varying compaction pressures and can be improved by reducing surface roughness, increasing chemical and structural homogeneity, and by alloying.

KEYWORDS: stainless steel 316, electrochemical corrosion, open-circuit potential (OCP), potentiodynamic polarization, polarization resistance, R_p , corrosion rate

1. Introduction

The use of stainless steels in various fields must take into account the conditions under which the material is to operate, namely the working environment, its temperature, and the nature and level of stress. Considering these aspects and other possible criteria (processing conditions and cost-effectiveness, availability), the set of operating properties required for the steel used is determined [1].

The chemical composition of austenitic stainless steel 316 can influence the mechanical properties and corrosion behaviour. Thus, chromium increases corrosion resistance, nickel, a gamma-forming element, stabilises the austenitic structure, ensures repassivation especially in reducing environments, and improves toughness at low temperatures. Molybdenum stabilises the resulting passive film, especially in combination with chromium, and improves resistance to pitting and crevice corrosion. It also improves oxidation resistance at high temperatures and mechanical properties at both low and high temperatures [2].

Since austenitic stainless-steel powders are obtained by water atomisation, they may have a carbon content higher than 0.03%. This improves high-temperature resistance but may lead to the development of pitting corrosion or intergranular

corrosion (caused by the precipitation of chromium carbides at the grain boundaries) [2, 3].

The presence of manganese can influence pitting corrosion behaviour, as it forms manganese sulphide in the presence of sulphur.

The presence of nitrogen in the structure of these steels increases strength and hardness, reduces ductility, but increases susceptibility to intergranular corrosion (as a result of the formation of chromium nitrides).

The presence of iron particles incorporated into stainless alloys can negatively affect corrosion resistance. These may originate from the supplier, during mixing with additives, from the die during pressing, from inadequate cleaning of the sintering furnace, or from processing or storage [2, 3].

The austenitic structure specific to stainless steel 316 provides resistance to the corrosive action of air, water, concentrated nitric, sulphuric, and phosphoric acids, and to creep. These steels are non-magnetic, have good weldability, but their machinability deteriorates due to work hardening [4, 5].

They are used in the chemical, petrochemical, food, aerospace, medical, transport industries, and household items [4].

The mechanical characteristics of stainless steel 316, according to MPIF, [3] are: tensile strength 280 MPa, yield strength 230 MPa, Young's modulus 105

GPa, Poisson's ratio 0.25, hardness 59 HRB, density 6.4 g/cm³.

The porous nature of sintered steels increases the tendency to corrosion (pitting, crevice corrosion, and their propagation). Thus, increasing the compaction pressure increases density and improves corrosion behaviour.

Also, increasing the sintering temperature from 1149 °C to 1316 °C results in increased sintering rate and densification, which leads to increased tensile strength, yield strength, hardness, impact resistance, and corrosion resistance. Sintering in a hydrogen atmosphere can increase densification and ductility as a result of oxide reduction [3].

The corrosion behaviour of sintered stainless steel 316 in various environments can be characterised using electrochemical tests. In this way, the electrochemical conditions present on the surface

of stainless steel exposed to a certain corrosive environment can be studied, the stability of passivity can be assessed, the types of corrosion and especially the danger caused by macroscopic and microscopic electrochemical cells due to differences in physical or chemical states between two points on the surface of a steel.

The purpose of the paper is to characterise the corrosion behaviour, in a 3.5% NaCl solution of sintered austenitic stainless steel 316.

2. Experimental conditions

The chemical composition of the austenitic stainless steel 316 powder used in the experimental research is shown in Table 1. It complies with the Metal Powder Industries Federation standards [3].

Table 1. Chemical composition of 316 powder

Steel brand	Chemical composition, %								
	C	Cr	Ni	Mo	Si	Mn	S	P	Fe
316	max 0.08	16 - 18	10 - 14	2 - 3	max 1	max 2	max 0.03	max 0.045	remaining
	0.03	17.1	12.09	2.5	0.51	0.84	0.012	0.03	remaining

The powder was obtained by water atomisation and has an irregular shape.

The powder had a measured hardness of HV_{0.05} = 939.6 MPa [6].

Pressing was carried out at ambient temperature. The compaction pressures were: for sample P1, F1 = 540 MPa; for sample P2, F2 = 628 MPa; for sample P3, F3 = 726 MPa; and for sample P4, F4 = 863 MPa [6].

Sintering was carried out at 1150 °C, with a holding time of 1 hour, followed by slow cooling. The microhardness after sintering was HV_{0.05} = 3120.2 MPa [6].

The microstructure of the obtained samples consisted of austenite. The average porosity of the stainless steel 316 compacts was determined using the line-intercept method and had the following values: sample P1 – 0.3178%, sample P2 – 0.2821%, sample P3 – 0.2153%, and sample P4 – 0.1272% [6].

Before the corrosion tests, the samples were mechanically polished to obtain lower surface roughness. This reduces deposits of solid materials, dust, rust, ferrous or other particles resulting from grinding or machining.

The metallographic analysis of the sintered stainless steel 316 samples subjected to corrosion in 3.5% NaCl solution was carried out using a Neophot 2 microscope with computer data acquisition.

Electrochemical studies were performed using a multi-channel electrochemical device, potentiostat/galvanostat system, OrigaLys France, OrigaFlex – model OGF+01A, and data acquisition was done using its OrigaMaster OM5 software. The electrochemical cell used was a classical three-electrode cell (working electrode – the tested material, reference electrode – Ag/AgCl with saturated KCl solution, potential versus NHE = +199 mV, against which all recorded potentials were measured, and counter electrode – a platinum electrode).

The samples subjected to corrosion tests were connected to a copper wire and then embedded in epoxy resin to obtain an active surface of approximately 1.6 cm².

The characterisation of corrosion behaviour was carried out using the following methods:

- monitoring the open-circuit potential (OCP) for 120 minutes, with a measurement interval of 0.6 s;
- potentiodynamic polarization testing, with measurement from -1.5 V to +1.5 V and a scan rate 1 mV/s;

3. Results and discussions

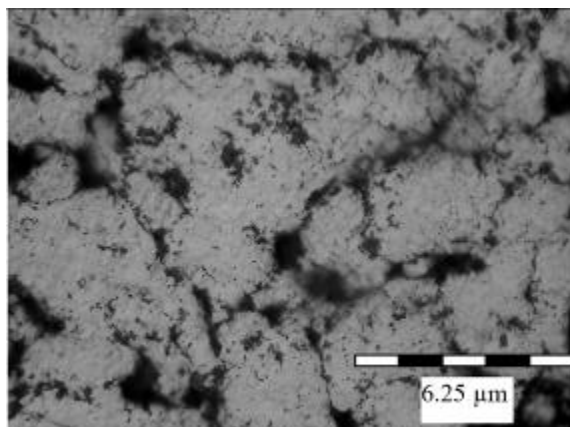
3.1. Metallographic analysis

In Figure 1 the microstructures of the sintered stainless steel 316 samples subjected to corrosion in

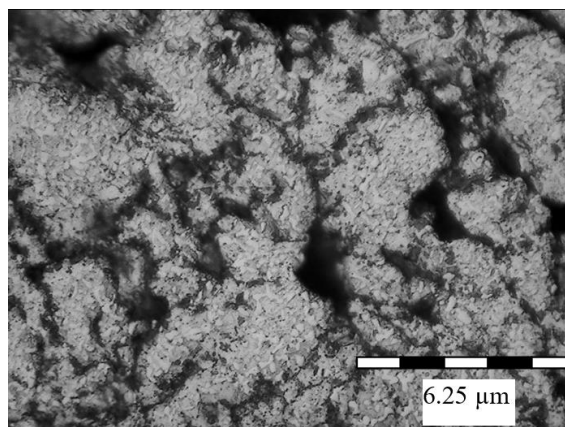
3.5% NaCl solution are shown, in both the unetched and electrolytically etched state with 50% HNO₃.

Analysing Figure 1, the presence of pitting corrosion can be observed. This is a form of localised attack, characteristic of passivable alloys, caused by the breakdown of the protective film due to the presence of aggressive anionic species, such as chloride ions. The chloride anion has high diffusivity,

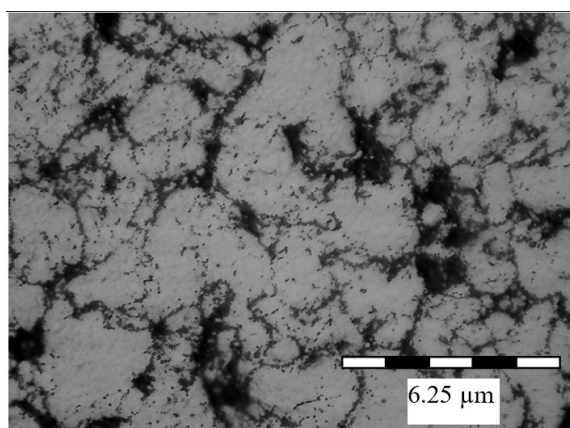
interferes with passivation, and is ubiquitous as a contaminant. A characteristic feature of this type of corrosion is that, on the surface of the alloy, along with intact passive areas, active points may appear simultaneously, without a protective film—meaning some areas with very low anodic current density (broad cathodic zones) and other smaller areas with higher current density (anodic zones).



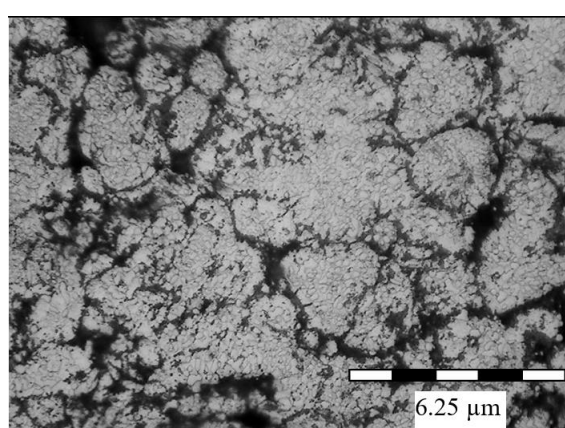
a - F1



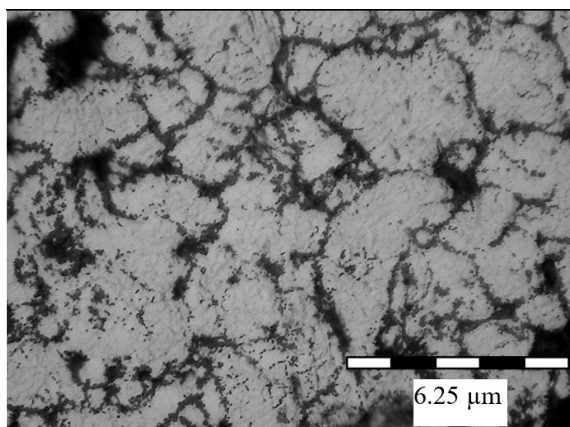
b - F1



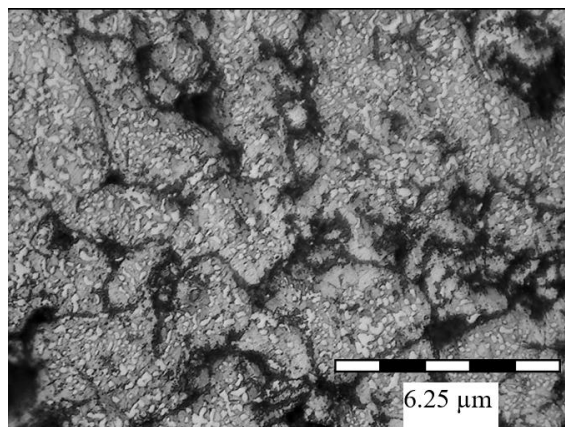
a - F2



b - F2



a - F3



b - F3

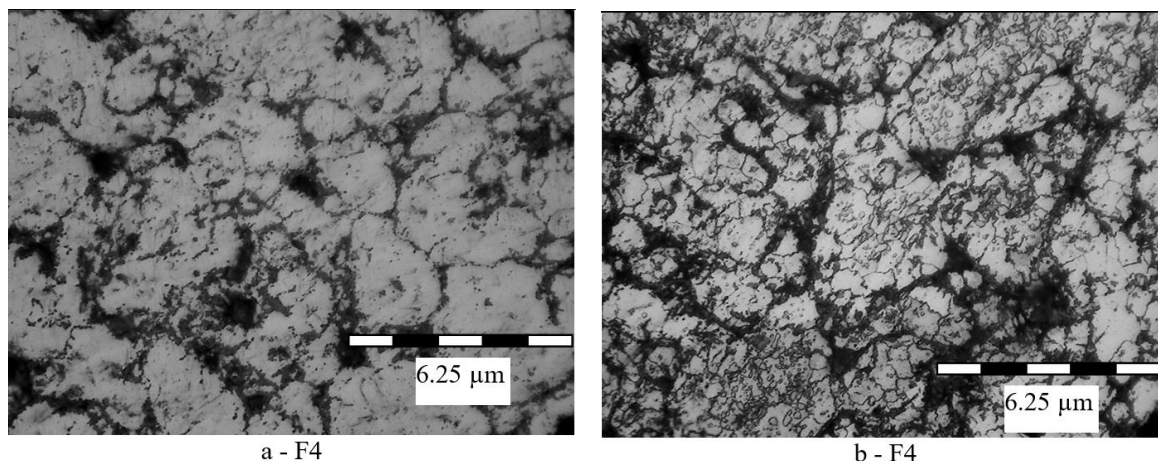


Fig. 1. Microstructure of sintered austenitic stainless steel 316 samples subjected to corrosion in 3.5% NaCl solution: a – unetched state; b – etched state, electrolytic etching with 50% HNO₃

Pitting corrosion is initiated at a certain chemical or physical heterogeneity on the surface, such as inclusions, secondary phase particles, precipitates segregated at grain boundaries, defects caused by mechanical processing, or dislocations.

Also, increasing the degree of surface processing through mechanical polishing enhances pitting corrosion resistance and ensures the formation of more compact, and therefore more protective films.

It is estimated that the tendency for pitting corrosion decreases with increasing chromium and nickel content in the alloy and by the inclusion of 2-5% molybdenum [1, 9].

By analysing Figure 1, intergranular corrosion can also be observed in certain areas. This manifests at grain boundaries where chromium carbides have precipitated, depleting the adjacent zones. It appears around the grains, develops in depth, and may sometimes lead to the disintegration of the steel.

Since carbon content plays an essential role in the occurrence of intergranular corrosion (due to carbide precipitation), it is estimated that reducing it to values lower than 0.03% decreases the steel's sensitivity to this type of corrosion. Also, adding stabilising elements to the steel that have a higher affinity for carbon than chromium such as titanium (in the ratio $Ti/C \geq 4$) or niobium (in the ratio $Nb/C \geq 8$) reduces susceptibility to intergranular corrosion [1].

3.2. Monitoring of open-circuit potential (OCP)

This is an electrochemical method that provides information on the corrosion behaviour of a material after immersion in a corrosive solution. It indicates the tendency of the material to interact with the corrosive environment.

Corrosion tests for each stainless steel 316 sample began with the monitoring of the open-circuit corrosion potential after immersion in the 3.5% NaCl solution, until a steady-state value was reached.

The duration of OCP monitoring was 120 minutes, to reach a steady-state value versus the Ag/AgCl reference electrode.

Figure 2 shows the time evolution of the open-circuit potential.

For sample P1 pressed with $F1 = 540$ MPa, an instability of the curve can be observed, specifically a decrease in the corrosion potential over the monitored interval, which can be attributed to the presence of chloride ions in the solution. This behaviour indicates a more active electrochemical state, caused by the infiltration of the solution into the open pores of the sample and the degradation of the passive film formed on the surface. A tendency towards stabilisation of the potential can be observed at a value of -412 mV, approximately 100 minutes after immersion.

For samples P2, P3, P4 pressed with forces $F2 = 628$ MPa, $F3 = 726$ MPa, $F4 = 863$ MPa, a stabilisation of the corrosion potential is observed after approximately 50 minutes of immersion. This indicates that a passive layer has formed on the analysed surfaces, which protects them from the action of the aggressive chloride ions in the electrolyte.

It can be noted that higher compaction pressures, around 863 MPa, ensure more noble (more positive) values of open-circuit potential, of -294.29 mV compared to the open-circuit potential values recorded for samples compacted at lower pressures, approximately -352.97 mV for a pressure of 628 MPa, and -393.48 mV for a pressure of 726 MPa.

The shift of the potential to more positive values with increasing compaction pressure shows the ability

of stainless steel 316 to develop a passive layer on its surface that reduces the corrosion process in the saline solution. The most positive potential, with a

high tendency to stabilise over time, corresponds to the sample compacted at 863 MPa.

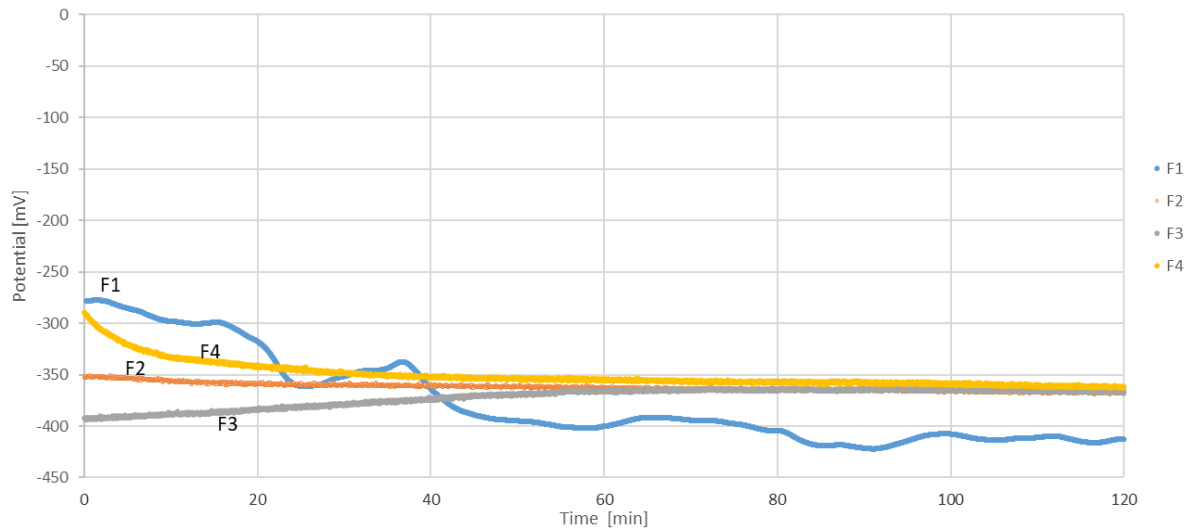


Fig. 2. Time evolution of open-circuit potential (OCP)

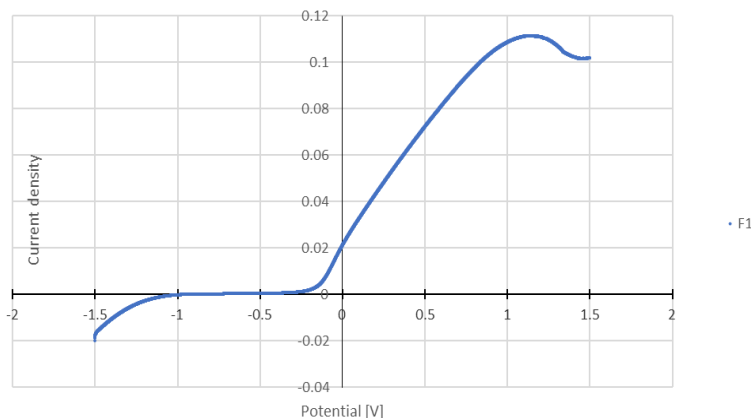
To increase the electrode potential and improve the passivity of the analysed samples, alloying with platinum and palladium can be carried out [3].

3.3. Potentiodynamic method – PD

For the successful use of a stainless steel, it is decisive whether in a certain corrosive environment it reaches the passive state, meaning whether the corrosion potential in an electrolyte decreases or not over a long period under these conditions. The shape of the current density – potential curves, Fig. 3 (depending on the steel grade and the corrosive environment), provides information about the corrosion kinetics.

From the analysis of the potentiodynamic polarization curves, especially from the analysis of the passivation domains, the anticorrosive performance of stainless steel 316 tested in contact with the corrosive environment consisting of 3.5% NaCl can be evaluated.

Passivity is the state of high corrosion resistance of stainless steels, under conditions in which they are thermodynamically active. This state is determined by the kinetic inhibition of the anodic metal dissolution process, through the shift of the potential to more electropositive values, accompanied by the formation of protective films. For each alloy and for each working condition, there is a current density value at which passivation occurs. Thus, the higher the current density, the shorter the time required to passivate the surface.



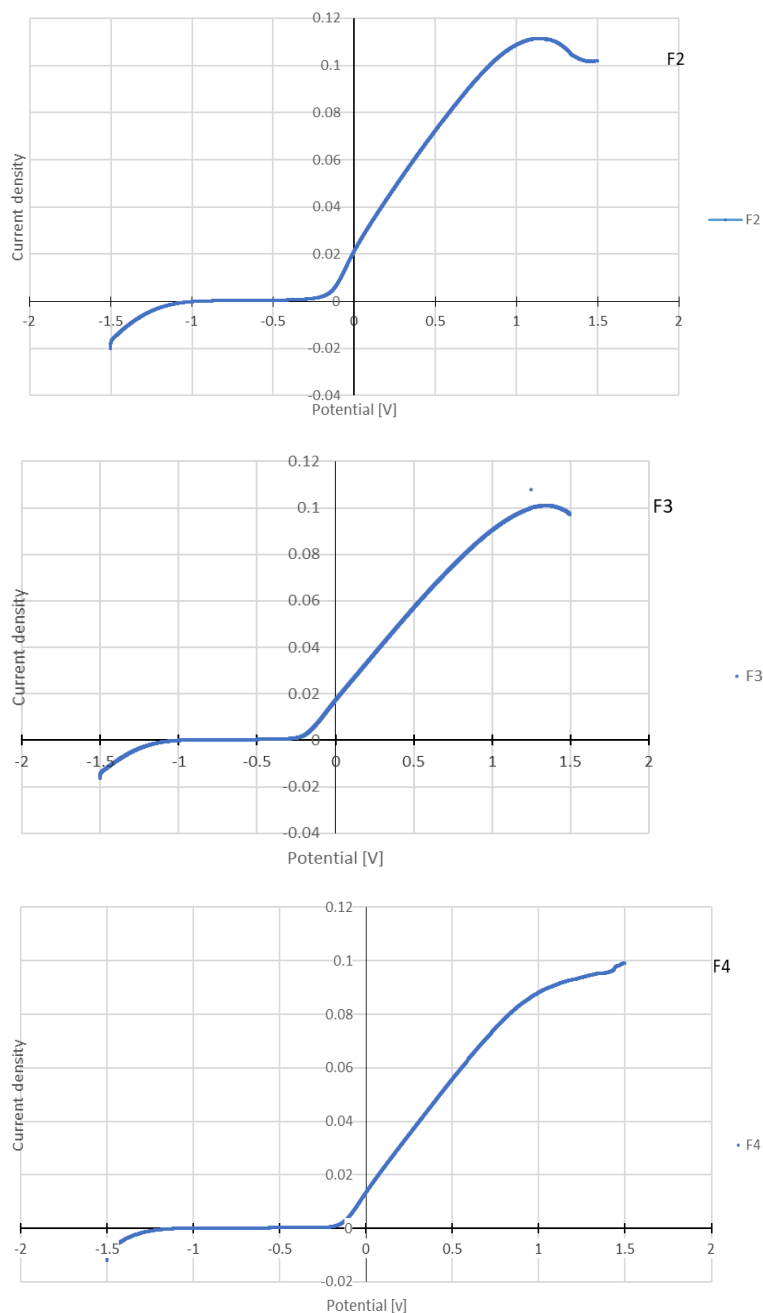


Fig. 3. Potentiodynamic curves

By analysing Figure 3, it can be observed that the highest current density of $0.0013 \mu\text{A}/\text{cm}^2$ corresponds to compaction with force F1, and the lowest current density of $0.0011 \mu\text{A}/\text{cm}^2$ corresponds to compaction with force F4. Thus, sample P1 with higher porosity passivates more quickly, while sample P4 with higher compactness passivates over a longer period.

By analysing Fig. 3, the presence of passivation plateaus can be observed, ranging from -1.0950 V to -0.2422 V for the sample compacted at a pressure of 540 MPa, and from -1.2448 V to -0.1459 V for the

sample compacted at a pressure of 863 MPa. Thus, it can be concluded that the stainless steel 316 samples resist corrosion over a wide potential range, which improves with increasing compactness. This aspect is due to the microstructure composed of austenite, a homogeneous solid solution that exhibits high stability in the saline environment.

Monitoring the temperature at which the corrosion process takes place is important because it can influence the corrosion rate. Thus, increasing the temperature can intensify the electrochemical reactions of the corrosion process and reduce the

concentration polarization of the cathodic reaction, which leads to the acceleration of the diffusion of the depolarizing agent and ions in the solution. The presence of Cl^- ions lead to the breakdown of the passivation films.

Monitoring polarization resistance is an electrochemical method for measuring corrosion, which provides information about the corrosion rate. Therefore, the higher the polarization resistance, the

lower the corrosion current, and the more resistant the alloy is to corrosion.

By analysing Figure 4, it can be observed that with the increase in compaction pressure from 540 MPa for sample P1 to 863 MPa for sample P4, the polarization resistance increases from $513.82 \Omega\text{cm}^2$ to $7119.22 \Omega\text{cm}^2$, which leads to an increase in corrosion resistance.

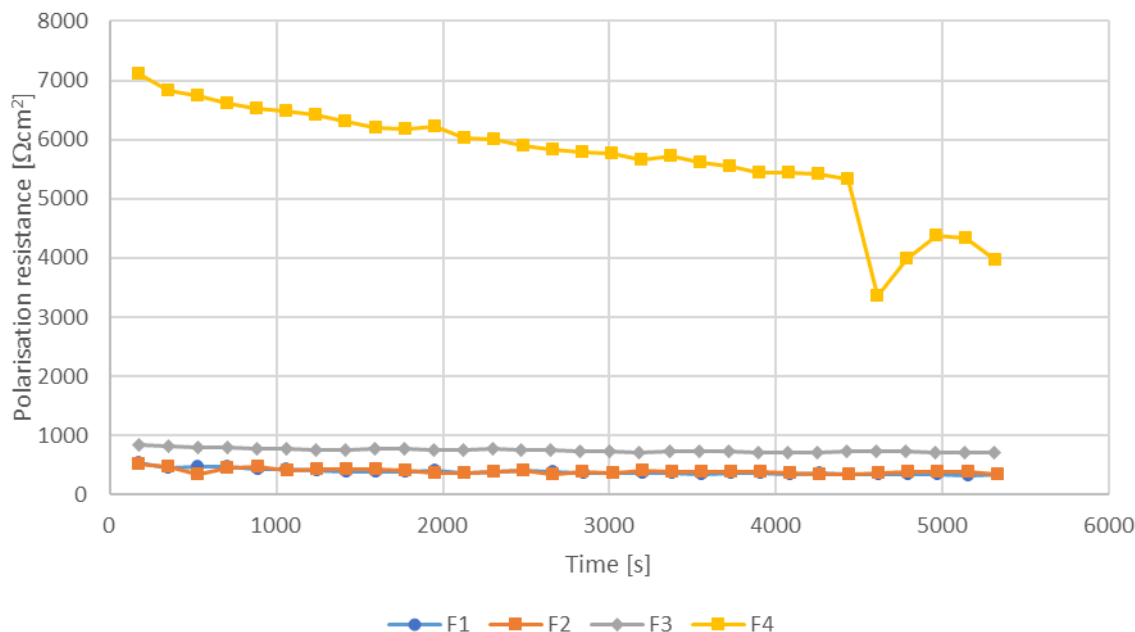


Fig. 4. Evolution of polarization resistance over time

Regarding the evolution of corrosion rate over time, shown in Figure 5, it can be seen that the corrosion rate is higher for samples P1 and P2, compacted at pressures of 540 MPa and 628 MPa,

and then begins to decrease with the increase in compaction pressure to 726 MPa for sample P3, and more significantly for sample P4 compacted at a pressure of 863 MPa.

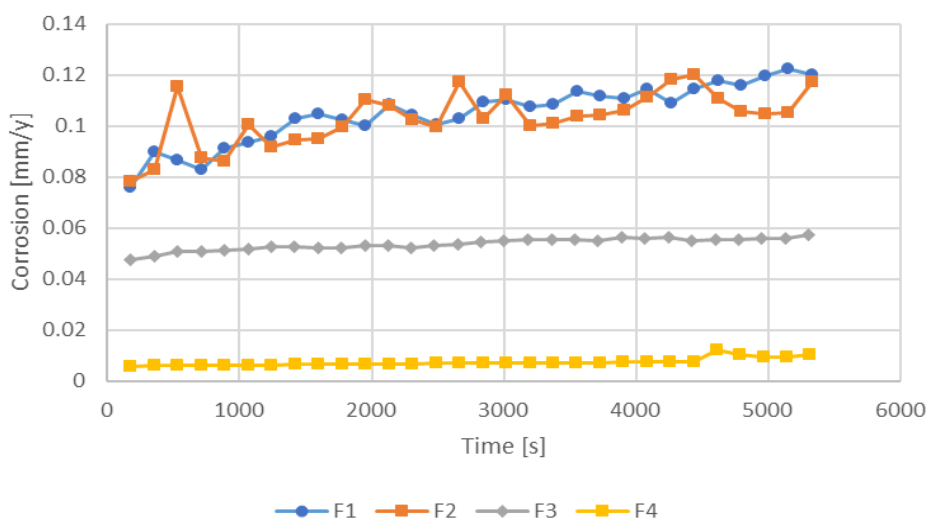


Fig. 5. Evolution of corrosion rate over time

Thus, with the increase in compactness of the samples, the corrosion rate decreases from 0.078 mm/year for sample P1 to 0.0056 mm/year for sample P4.

An improvement in the corrosion resistance of the analysed stainless steel 316 can be achieved by reducing open porosity and increasing compactness. Thus, chemical passivation treatments, sintering with the presence of a liquid phase, double pressing and double sintering, injection moulding, the addition of alloying elements such as molybdenum up to 5%, alloying with titanium and niobium or with copper and tin up to 1.5% can significantly improve corrosion resistance.

In liquid-phase sintering, the use of additives such as 0.2% B, 1% BN, 1% NiB, 1% CrB with particle sizes of 38 μm leads to the formation of dense microstructures, thus improving corrosion resistance [9].

Increasing the sintering temperature from 1150 $^{\circ}\text{C}$ to 1250 $^{\circ}\text{C}$, as well as the sintering time from 30 minutes to 240 minutes, results in the reduction of open pores and the content of carbon, oxygen, and nitrogen, thereby improving corrosion resistance. Increasing cooling rates up to values of about 200 $^{\circ}\text{C}$ can ensure a reduction in corrosion rates due to the formation of homogeneous structures [9].

If high porosity is required, as in the case of filters, it has been found that infiltration with copper and bronze can lead to an improvement in corrosion resistance [9].

4. Conclusions

When assessing corrosion behaviour, one must take into account the influence of crystalline defects, as well as the fact that in industrial processes the surface contains impurities that become cathodic zones and is mechanically and structurally altered, thus creating areas with higher energy that will tend to corrode, becoming anodic zones, thereby affecting and reducing corrosion resistance.

Following the conducted research, the following conclusions can be formulated:

- the metallographic analysis performed on the sintered stainless steel 316 samples subjected to corrosion in 3.5% NaCl solution reveals both pitting and intergranular corrosion; pitting corrosion is reduced by lowering surface roughness through mechanical polishing, thus also limiting contamination and improving the chemical and structural homogeneity of the alloy; increasing the

chromium, nickel, and molybdenum content improves resistance to pitting corrosion;

- intergranular corrosion is limited by reducing the carbon content in the steel below 0.03% and by introducing alloying elements such as titanium or niobium, which prevent the formation of chromium carbides at the grain boundaries;

- as the compaction pressure increases, the electrode potential and its tendency to stabilise over time also increase;

- from the analysis of the passivation domains, it can be concluded that the stainless steel 316 samples resist corrosion in 3.5% NaCl solution over a wide potential range, which improves with increasing compactness; this is due to the passive layer formed on the surface of the samples, which reduces corrosion in the saline solution;

- samples with higher porosity passivate over a shorter time but over a smaller potential range;

- with the increase in compaction pressure from 540 MPa for sample P1 to 863 MPa for sample P4, the polarization resistance increases from 513.82 Ωcm^2 to 7119.22 Ωcm^2 , which leads to increased corrosion resistance;

- with the increase in compactness of the samples, the corrosion rate decreases from 0.078 mm/year for sample P1 to 0.0056 mm/year for sample P4;

- the corrosion resistance of stainless steel 316 samples in 3.5% NaCl solution can be improved by reducing open porosity, increasing compactness, and alloying.

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