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Electrochemical Behavior of stainless steel AISI 430 exposed to simulated food

Anderson Sandoval-Amador[1], Jhon Edisson Torres-Ramirez[2], Diana Yiseth Vargas-Castro[1], Jhonatan Ramiro Caceres-Nuñez[1], Hugo Armando Estupiñan-Duran[3], Darío Yesid Peña-Ballesteros[1]

[1] Grupo de Investigaciones en Corrosión GIC, Universidad Industrial de Santander UI, Bucaramanga, Colombia.
e-mail: anderson84f@gmail.com, dypena@uis.edu.co
[2] Comisión Nacional de Energía Atómica, Universidad Nacional de San Martin, Buenos Aires, Argentina.
e-mail: jtorram@gmail.com
[3] Grupo de Tribología y Superficies GTS, Universidad Nacional, Medellín, Colombia
e-mail: haestupinand@unal.edu.co

ABSTRACT

Due to the excellent properties of stainless steel, these materials have a variety of applications among which is the food processing industry. One of the main problems in this industry is the possible releasing of metal ions towards food. For this reason, it is very important to know corrosion behavior of steels that are used in this industry. In this study the release of Fe, Cr and Ni ions and the electrochemical behavior of AISI 430 steel with three different surfaces finishes in contact with a solution that simulates food contact (acetic acid 3% v / v) was evaluated. For this, the influence of the surface finish (polished by SiC paper 600, 1200 and 1500 grit) and the exposure time to the solution (4 and 10 days) at different temperatures (25, 60 and 100°C) was analyzed by atomic absorption spectroscopy, linear polarization resistance and potentiodynamic polarization curves. The results show that the releases of Fe, Cr and Ni ions, the linear polarization resistance and the corrosion rate of the AISI 430 steel depend on surface finish and temperature. The lower corrosion rate was obtained when the material had the smooth surface finish, in such a way that it is possible to avoid health risks due to the release of metal ions.

Keywords: Metal release, surface finish, acetic acid, food contact, corrosion.

1. INTRODUCTION

Stainless steel has excellent properties, which include high corrosion resistance at high and low temperatures, mechanical and physical properties, durability, easy cleaning and recycling It, is also aesthetically attractive since it can keep its luster and natural color. For that reason, stainless steel has a wide range of applications ranging from skyscrapers, medical implants to diverse food-related applications.

In applications where stainless steel comes into direct or indirect contact with human, such as food processing, required a wide variety of studies that allow to understand the performance that these materials will be at the time to be put into service [1-4]. Therefore, for the food industry the study of the performance of stainless steels which are in contact with food is of a great interest, since it may lead to leaching of metal ions to food and this will cause adverse effects on human health [5]. According to the above, several works have been developed in order to understand the behavior of stainless steel in contact with food [6-12].

The Italian Ministerial Decree of March 21, 1973 is one of the more detailed documents on the regulation of the global release of metal ions. According to this text, the most relevant components of stainless steel, whose release must be considered to be in contact with food are Fe, Cr and Ni [13].

Chromium is an essential element necessary for the metabolism of fats and sugar. The daily dietary intake of Cr (III) estimated is 50 to 200 µg for human, and there are no toxic effects documented in nutritional studies at levels of up to 1 mg per day. The World Health Organization (WHO) has established the Cr (IV) maximum value at 0.05 mg/L in drinking water due to the Cr (IV) be carcinogenic [5, 12, 14, 15].

Nickel is a key component of stainless steels, specially austenitic and duplex ones, whose effects on human health are mainly related to allergic reactions. The average daily intake of Ni is estimated around 0.2 mg/day [5, 12, 15, 16].

According to the Italian Decree, it is possible to use a 3% v / v acetic acid solution to simulate contact

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with food. For this reason, to carry out this study, this solution was used as electrolyte in the ion release tests and the electrochemical tests to determine the corrosion behavior of AISI 430 steel.

2. MATERIALS AND METHODS

2.1. Sample preparation

Samples were cut from AISI 430 steel with approximate dimensions of 20 mm x 20 mm x 0.45 mm. The grinding was performed using SiC abrasive paper, manufactured by Buehler, Germany, designated as 600 grit, 1200 grit, and 1500 grit. Finally the samples were cleaned with ethanol in an ultrasonic bath for an approximated time of 14 minutes and dried with air.

2.2. Immersion test

Immersion tests were conducted in two steps. These conditions are based on Italian decree (D.M. 21-03-1973) and the procedure described by G. Herting et al. [12]. In the first step, the samples of AISI 430 steel with three different surface finishes were immersed in simulated food at 25°C and 60°C and left exposed during 4 to 10 days. In the second step, samples with the best surface finish (1500 grit) were immersed in the solution at temperature of 100°C, for this stage the immersion time was 5 min, 15 min, 30 min, 60 min and 90 min.

2.3. Analysis of Fe, Cr and Ni release ions

In order to determine the concentration of Fe, Cr and Ni ions released from AISI 430 steel, the final solutions obtained after immersing tests were analyzed by atomic absorption spectroscopy. The equipment used was a spectrum photometer Buck Scientific 210VGP.

2.4. Electrochemical test

To determine the electrochemical behavior of AISI 430 steel in contact with simulated food, the linear polarization resistance, and potentiodynamics polarization tests were performed. A potentiostat/galvanostat Gamry PC4 750 was used for this purpose. The tests were performed in a classic three-electrode cell configuration. AISI 430 steel was used as working electrode; a platinum mesh was a counter electrode and an Ag/AgCl (3M KCl) as a reference electrode. The electrolytic solution was acetic acid 3% v/v. The working area was 0.78 cm^2. In all cases the cell was sealed to prevent leaks and evaporation of the solution. The working temperature of the electrochemical tests was 25±1°C and 60±1°C.

2.5. Surface analysis

The morphology of the surface of AISI 430 steel and the damage generated by contact with simulated food was observed using scanning electron microscope Quanta FEG 650.

3. RESULTS AND DISCUSSION

3.1. Characterization of steel AISI 430

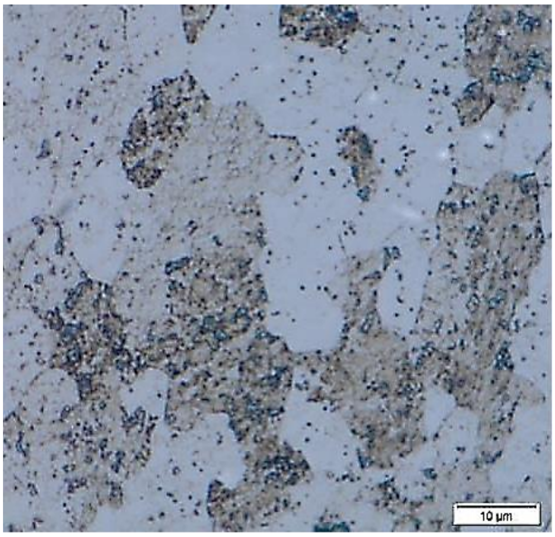
Table 1 presents the composition of AISI 430 steel which was obtained through optical emission spectroscopy OES.

Table 1: Chemical composition of steel AISI 430 obtained by OES (% mass).

	C	Mn	P	S	Si	Cr	Ni	Fe
430 SS	0.096	0.512	0.02	<0.150	0.338	16.7	0.256	81.22

After proper surface preparation, a chemical attack of the alloy was performed, using an acid solution with 10 mL of glycerin, 30 mL of HCl and 30 mL of HNO_3 for an approximate time of 2 min according to the definitions given in the standard ASTM E-407. The microstructure was observed using an optical microscope Olympus GX71. As can be seen in the figure 1, the microstructure of the studied steel presents some inclusions and grains of ferrite with indistinct edges of grain. This result can be attributed to the cold rolled microstructure was mainly characterized by the deformed ferrite grains.

Figure 1: Steel AISI 430 microstructure



3.2. Release of ions of Fe, Cr and Ni

Atomic absorption (AA) spectroscopy analyses were performed with the final solutions of immersion test to obtain the Fe, Ni and Cr ion concentration in each of the stages carried out. The results obtained are shown in the Table 2 and Table 3. The differences in the release of Fe, Ni and Cr ions in immersion test can be used to describe the influence of the surface finishing of stainless steel in the releasing process. The obtained data clearly show that the finish with higher roughness (600) presented the greatest release of metal ions and with the lower roughness (1500) the minor release. It should emphasize that the release of Ni and Cr ions was only occurred for surface finishes of 600 and 1200. The correlation found between the ion release and the surface finishing is according to the reported previously in the literature [12, 17].

Table 2: Released metallic ions at 25°C and 60°C after a exposure time of 10 days.

T (°C)	Finish	Fe (ppm)	Ni (ppm)	Cr (ppm)
25	600	0.4026	--	--
25	1200	0.3305	--	--
25	1500	0.2872	--	--
60	600	1.2549	0.1329	0.0961
60	1200	0.8244	0.1061	0.0593
60	1500	0.8093	--	--

The release of metal ion process is also time dependent (see Table 3). The data show changes in release rates during times of 5, 15, 30, 60 and 90 minutes at 100°C. Similar results have been reported by Herting et al. [12,17]. This behavior can be attributed to the formation and dissolution of a thin layer of chromium oxide that temporarily protects the material.

Table 3: Released metallic ions at 100°C.

time (min)	Fe (ppm)	Ni (ppm)	Cr (ppm)
5	0.7558	--	0.0119
15	0.4861	--	--
30	0.6128	--	--
60	0.7095	--	--
90	0.6236	--	0.0175

3.3. Electrochemical behavior

The results of the polarization resistance tests are shown in Table 4. As can be seen at temperature of 25°C samples of AISI 430 steel in contact with simulated food presented the highest values of polarization resistance. These results are consistent with the results obtained in similar releasing tests reported by the literature in which the lowest metal ions release occurs at room temperature [12]. On the other hand, samples exposed to the test solution at 60°C presented an increase in the polarization resistance with the immersion time, which shows an inverse relationship between corrosion resistance and the release of ions. This may be associated with the formation of a layer of chromium oxide that protects the material from corrosion, which is consistent with that reported in literature [1,12,17,18].

Table 4: Linear polarization resistance values of AISI 430 steel in contact whit simulated food.

Temperature °C	Finish	time (days)	Rp (kΩ/cm^2)
25	600	10	69.0
25	1500	10	1060.0
60	600	4	15.2
60	1500	4	54.1
60	600	10	34.0
60	1500	10	64.10

Figures 2 and 3, Present the potentiodynamic polarization curves which show the corrosion susceptibility of the studied material in a simulated food solution. As can be seen, the material has a same trend for all studied conditions, which is very similar to that reported by Fattah-alhosseini and Vafaeian in [19] where the corrosion behavior of AISI 430 steel in contact with acidic media was studied.

In Figure 2, the effect of the immersion time in the electrochemical behavior of AISI 430 steel exposed to the simulated food at a temperature of 25°C can be seen. The samples exposed for 10 days have displacements for the corrosion potential, the active-passive transition potential and the pitting potential regarding samples exposed for 4 days. Passive region of the samples exposed for 10 days is more stable, which is observed in a wider potential gap with respect to the samples exposed for 4 days.

The effect of temperature on the electrochemical behavior of AISI 430 steel exposed to simulated food for 10 days can be seen in Figure 3. In this figure can be seen that the metal dissolution process is accelerated by exposing the steel at a temperature at 60°C, therefore less energy is required to achieve the breakdown of the passive layer. Likewise, can be seen a shift to the right in the current density of the samples exposed to 60° C. Also, the surface finish has an effect on the corrosion rate, since, These surface irregularities generated by grinding process cause a significant increase in surface roughness and consequently an increase in the contact area with the medium, which should have contributed to the decrease in corrosion resistance [20].

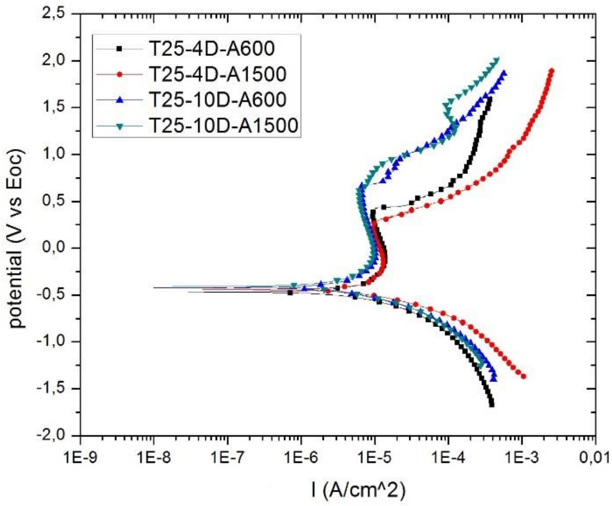


Figure 2: Potentiodynamic curves of AISI 430 steel in contact with simulated food obtained at 25°C.

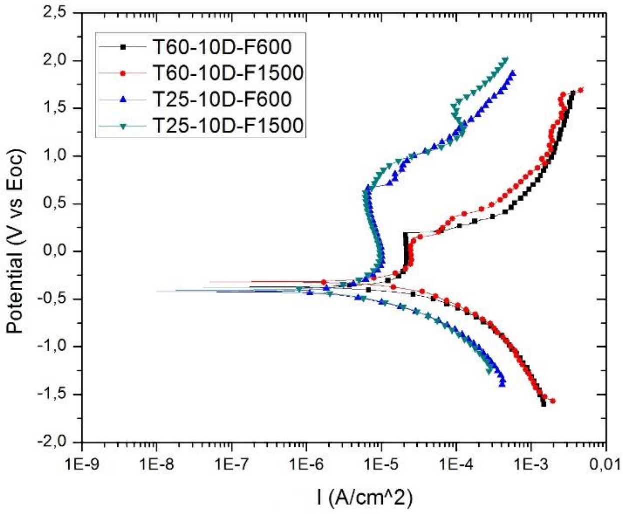


Figure 3: Potentiodynamic curves of AISI 430 steel in contact with simulated food obtained at 25 and 60°C after 10 days of immersion.

From the potentiodynamic curves of Figure 3 the corrosion rate was calculated applying the Tafel method on the cathodic zone (table 5). As can be seen, the higher corrosion rate occurred in AISI 430 steel with surface finish 600 samples, this is regarding to the largest exhibition area presenting these samples. Similarly, can be seen, that the corrosion rates increased with the temperature increase. These results correlated with that found in the test of ion releasing, where it was found that higher temperatures increased amount of released ions [12].

A characterization of the surface of tested samples was performed in order to establish the type of occurred damage. It was found that the main mechanism of corrosion was pitting as illustrated in Figure 4 which presents the surface of the samples tested at 25°C with different surface finishing and exposure times. The samples with surface finish of 600 exposed for 4 days shows a higher number of pits (Figure 4a) that the same sample exposed for 10 days (Figure 4C). These results confirm the obtained conclusions from polarization curves (see Figure 2). The same conclusion is true for the samples with surface finish 1500 (Figure 4b and 4D).

Table 5: Corrosion rates of AISI 430 steel in contact with simulated food.

Temperature °C	Finish	time (days)	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	V_{corr} (mpy)
25	600	10	-422	2.700152	0.020806
	1500		-407	0.179215	0.001381
60	600	10	-374	2.720299	0.020961
	1500		-319	0.803517	0.006191

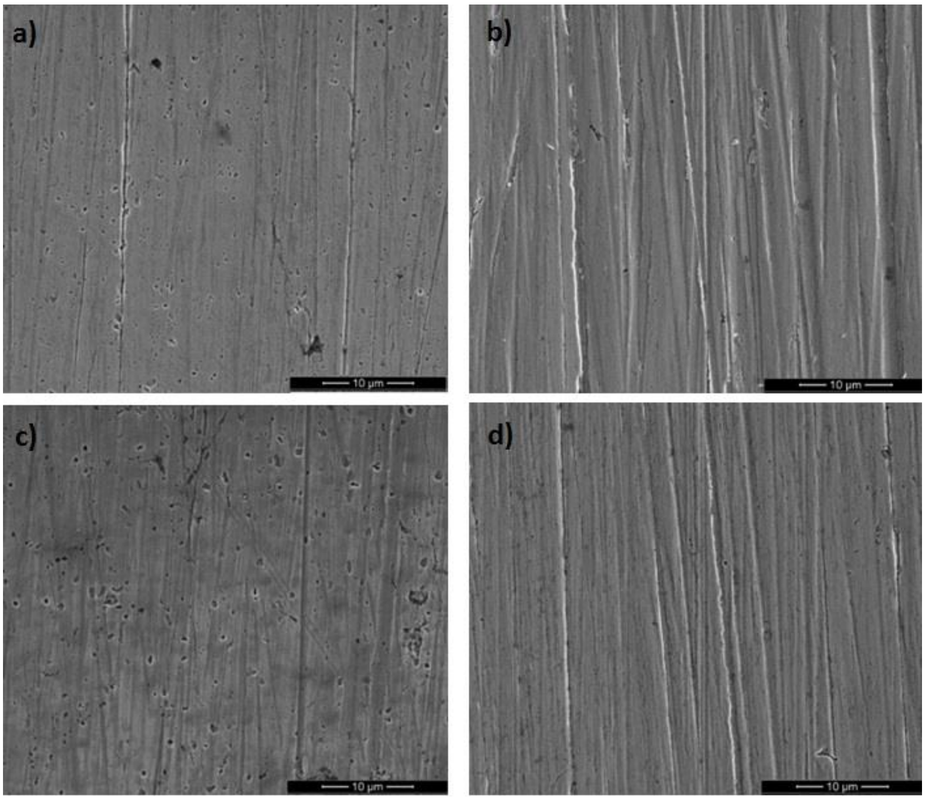


Figure 4: SEM micrographs of AISI 430 steel in contact with simulated food at 25 °C. a) finish 600 – 4 days, b) finish 1500 – 4 days, c) finish 600 – 10 days d) finish 1500 – 10 days.

4. CONCLUSIONS

The results of atomic absorption spectroscopy showed that the release of ion increased with the increase with the increase of the alloy roughness and test temperature. Samples with surface roughness (finish 600 grit) and temperature of 60°C showed higher release with respect to the glossy surface (finish 1500 grit), due to the rougher surface would be easily pitted because the smooth surface has fewer places for pit nucleation and can quickly form a passive film preventing pit nucleation.

The highest chromium release was observed at a working temperature of 60°C, however, It does not exceed the permitted limit, 0.1 mg/L according to Italian decree. The electrochemical obtained results showed the effect of the temperature and roughness in increasing of the corrosion rate. In addition, it was found that the immersion time shifts the pitting potentials, which increase the corrosion in AISI 430 steel.

Steel AISI 430 is appropriate to be used in applications involving food contact, provided to ensure a fine surface finish and to avoid the exposure to high temperatures for prolonged times.

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