STUDY OF CORROSION BEHAVIOR OF AISI304 STAINLESS STEEL SAMPLES USING ACCELERATED ELECTROCHEMICAL METHODS

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Abstract: *The aim of this work was the study of corrosion behavior of the AISI304 stainless steel samples in 3%, 6% and 9% acetic acid solutions, using accelarated electrochemical methods. In order to achieve accelerated corrosion tests was been used a system consisting of a potentiostat-galvanostat Wenking HP 96-20, an electrochemical cell, two multimeters Hameg HM 8112-3 for monitoring the voltage values and a PC system for programming, command, acquisition and interpretation of the values recorded on the multimeter.*
In order to developing the mass balance of the migration process of metal ions were calculated the theoretical masses of ^{56}Fe, Mn, Cr and Ni ions migrated in the acidic simulant solutions. Chemical analysis of corrosive solutions, after carrying out the electrochemical tests, was carried out using ICP-MS method. Were calculated the dissolution rates η for each metal ion studied. Regarding the corrosion behavior of metal ions in corrosive solutions was observed a decrease of dissolution rate with the increasing of acetic solution concentration.

Keywords: *electrochemical cell, stainless steel, acetic acid, mass balance, dissolution rate*

1. Introduction

In this paper was used an advanced method to study the transfer of heavy metal ions from stainless steel samples intended to come into contact with the food simulated environments, using in addition to a corrosive environment concentration gradient and the current gradient resulting from the application of continuous current to the electrodes, both formed of the same stainless steel studied. Given that one of the most aggressive environments of food processing industry is the acid environments [1], [2], [3], [4], [5], and taking into account the pH values encountered in current industrial practice

(wine industry, vinegar or canning industry), in the tests presented in this paper, as food simulant corrosive environments, acetic acid in double distilled water solutions (simulant B) was used [6], [7], [8], [9].

The aim was to increase the dissolution rate with direct effect on the limit of detection of heavy metal ions in the food environment, the accuracy of measurement of the concentration of metal ions and analytical research on productivity growth by reducing the time required for corrosion and diffusion process. To accomplish the intended purpose, has been developed the material balance of metal elements that dissolve in acidic food simulant solutions

by determining the theoretical and real masses of iron, manganese, chromium and nickel ions.

2. Materials and methods

2.1. Metallic samples, corrosive environments and equipments

To study the corrosion behavior of the AISI304 stainless steel were used discs with a diameter of Ø40 and 1 mm of thickness. Chemical composition of metal samples are shown in the Table 1 (according to EN 10088-2:2005) [10].

To achieve accelerated corrosion tests were used a system consisting in a potentiostat-galvanostat - model Wenking HP 96-20 (Bank Elektronik, Germany), a thermostated electrochemical cell with an working and a counter electrode, both of the stainless steel subjected to the corrosion tests, two multimeters HM8112-3 (Hameg, Germany) for monitoring the voltage values and a PC system for programming, command, acquisition and interpretation of the values recorded on the multimeter. (Figure 1).

Chemical analysis of corrosive solutions, after carrying out the electrochemical tests, were been carried out using ICP-MS method (*ICP-MS Agilent 7500*).

Table 1.
Chemical composition of AISI304 stainless steel [wt %]

Fe	C	Mn	P	S	Si	Cr	Ni
67	0.07	1-2	0.045	0.03	1	18	8
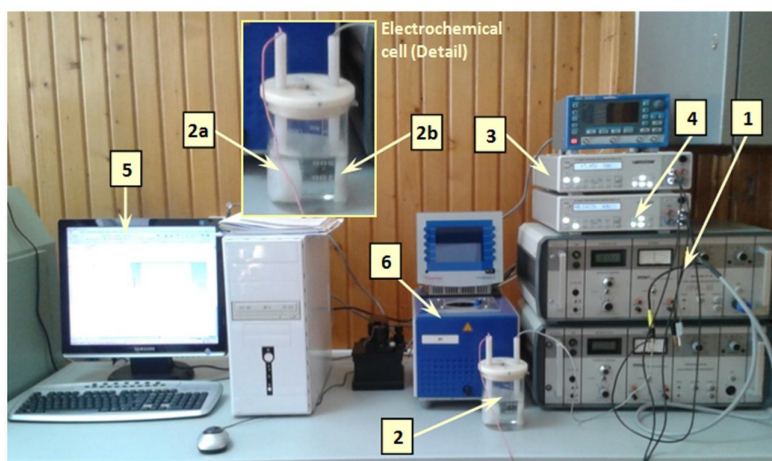
Figure 1. Potentiostat-galvanostat system for studying the corrosion behavior of AISI304 stainless steel samples: (1) - potentiostat-galvanostat Wenking HP 96-20 (Bank Elektronik, Germany); (2) – electrochemical cell; (2a) – working electrod - disk Ø40 (AISI304 stainless stell); (2b) – counter electrod - disk Ø40 (AISI304 stainless stell); (3) - Hameg HM8112-3 multimeter for working voltage monitoring; (4) - Hameg HM8112-3 multimeter to record the current intensity values in the electrochemical cell; (5) - PC system for programming, command, acquisition and interpretation of the values recorded on the multimeter (4); (6) - thermostatic bath (Therm Phoenix II)

2.2. Experimental conditions and methods

The experimental conditions used for the electrochemical tests, in each of the three food simulant corrosive environments, are shown in the Table 2. The volume of the electrolyte solutions was 300 ml. The exposure time of the metal samples in corrosive environments was 90 min.

Tabel 2.
Experimental conditions used to perform the electrochemical tests

Concentration of CH₃COOH solutions, [%]		
3	6	9
Tensions in electrochemical cells, [V]		
6	7	6.5
Temperature of electrolyte solutions, [ºC]		
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2.3. Developing material balance

In order to developing the mass balance of the metal ions migrated from the AISI304 stainless steel samples, the theoretical and real masses of ^{56}Fe, Mn, Cr and Ni ions in acidic simulant solutions were determined. To calculate the theoretical mass of metal ions dissolved, the equation (1) was used, using weighted atomic mass (A_p) (3), based on the ion concentration in the studied stainless steel.

$$m = k \cdot I \cdot t \qquad (1)$$

where,
m - amount of metal dissolved from the anode, [g];

k – gram equivalent (electrochemical equivalent) of the species;
I - the measured intensity of the electric current in the electrochemical cell [A];
t - time of electrolysis, [$min.$].
Gram equivalent of the metal was calculated using the relation (2):

$$k = \frac{A_p}{z \cdot F} \qquad (2)$$

where,
A_p - weighted atomic mass of the species studied, [g];
z - valence species (the number of electrons involved in the reaction);
F - Faraday's constant ($F=96500$ $C/g.$ $echiv.$).

$$A_p = \frac{A_{Fe} \cdot \%Fe + A_{Mn} \cdot \%Mn + A_{Cr} \cdot \%Cr + A_{Ni} \cdot \%Ni}{4} \qquad (3)$$

Calculated masses of the dissolved metal ions in the solution were used to develop the theoretical mass balance.
For developing of the real mass balance, the simulant solutions were analyzed by ICP-MS.
For the calculation of the dissolution rate (η) was used the relation (4):

$$\eta = \frac{m_p}{m_t} \qquad (4)$$

where,
m_p - practical masses calculated by the equation (5), obtained by the ICP-MS analysis (concentration of the electrolytic bath after 90 min.), [g];
m_t – theoretical masses calculated by relation (1), [g].

$$C = \frac{m_p}{V} \rightarrow m_p = C \cdot V \qquad (5)$$

where,
C - concentration of metal species, [ppb];
V - volume of test solution, [ml];

3. Results and Discussion

Anodic current intensity values measured with the Hameg HM8112-3 multimeter reflect the anodic dissolution kinetic of the ^{56}Fe, Mn, Cr and Ni metal ions from the AISI304 stainless steel samples at 90 min. exposure time (Table 3).

Table 3.
The electric current values of the AISI304 stainless steel samples in 3%, 6% and 9% CH₃COOH solutions

Exposure time, [min.]	Current values, [A]		
	3%	6%	9%
90	0.1038	0.1522	0.1765

The masses theoretically dissolved, calculated using the relation (1), provided that the dissolution rate would be 100%, for the metal ions of the AISI304 stainless steel samples studied are shown in Table 4.

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Table 4.
Theoretical masses possible to be dissolved of metal ions in acidic simulant solutions from AISI304 stainless steel samples (after 90 min.), [g]

Elem. Conc.	^{56}Fe	Mn	Cr	Ni
3%	0.0381	0.0381	0.0254	0.0381
6%	0.0558	0.0558	0.0372	0.0558
9%	0.0647	0.0647	0.0431	0.0647

The values of real mass dissolved [g] of the of metal ions studied, found in food simulant acid solution, obtained by analyzing the solutions through ICP-MS method are shown in Table 5.

Table 5.
Real masses dissolved of the metal ions in acidic simulant solutions from AISI304 stainless steel samples (after 90 min.), [g]

Elem. Conc.	^{56}Fe	Mn	Cr	Ni
3%	0.0001	0.0016	0.0146	0.0025
6%	0.00018	0.0017	0.0198	0.0027
9%	0.0001	0.0017	0.0199	0.0028

By determining the theoretical and real masses values of ^{56}Fe, Mn, Cr and Ni ions, were calculated the dissolution rates η [%] (relation 4). The values of the dissolution rates are shown in Table 6.

Tabel 6.
The dissolution rates of the metal ions in the solution with the concentrations: 3%, 6% and 9% CH₃COOH [%]

	η_{56Fe}	η_{Mn}	η_{Cr}	η_{Ni}
3%	0.0026	0.0420	0.5748	0.0656
6%	0.0032	0.0305	0.5323	0.0484
9%	0.0015	0.0263	0.4617	0.0433

After obtaining the numerical values of the dissolution rate, can be achieve a comparative study that can provide informations on the influence of the solution concentrations on the dissolution rate of the metal ions in acidic food simulant solutions.

Regarding the corrosion behavior of metal ions in corrosive solutions is observed a decrease of dissolution with the increasing of solution concentration.

Because the migration of nickel ions in solution shows a great interest, the study of corrosion behavior by electrochemical methods has been the main purpose of this research. From studying the dissolution rate of nickel ions in the three solutions, we can observe that the maximum value was obtained at 3% CH₃COOH solution (*0.0656*), and the minimum value was obtained at 9% CH₃COOH (*0.0433*).

4. Conclusions

It may be noted that the electrochemical method used to study the behavior of AISI304 stainless steel in acidic environment, studied and presented in this paper, is less expensive and a fast tool that provides very accurate information about the nature of migration processes of metal species in corrosive solution. The obtained data make possible the development of the theoretical material balance, results that have been used with those obtained by ICP-MS analysis method for the calculation of the dissolution rate of metallic ions in the acid simulant solutions. The experiments performed on AISI304 stainless steel samples, in accelerated corrosion conditions using an electric gradient overlapped on the concentration gradient, have validated the validity of the method and also recommended for use in similar research. The higher dissolution rate increases the spectrometric analytical method sensitivity in very low concentration fields of heavy metals, with direct effect on the limit of detection and precision of determination.

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