ACCELERATED ELECTROCHEMICAL METHOD FOR STUDYING THE CORROSION BEHAVIOR OF AISI321 STAINLESS STEEL FOOD GRADE IN ACIDIC FOOD ENVIRONMENTS

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Abstract

The purpose of this research was to study by electrochemical methods the behavior of AISI321 stainless steel food grade samples in acidic corrosive environments. 3%, 6% and 9% CH_3COOH solutions in bidistilled water were used. The volume of solution studied was 300 ml. The exposure time of the stainless steel samples was 90 min. and the exposure temperature was $22\pm1°C$. In order to achieve the proposed objective was been used a complex system consisting of a potentiostat-galvanostat Wenking (HP 96-20), two multimeters Hameg (HM 8112-3) for voltage monitoring, an original electrochemical cell and a computer for programming, acquisition and interpretation of experimental data. In order to develop the mass balance the theoretical masses of ^{56}Fe, Mn, Cr, Ni and Ti metal ions which migrated in corrosive solutions were calculated. The chemical analysis of corrosive solutions after migration tests was performed by ICP-MS method. The dissolution rates of metal ions studied were calculated. The results obtained demonstrate the validity of the accelerated electrochemical method in laboratory tests for the study of the migration phenomena of metal ions in acidic food environments.

Key words: stainless steel, electrochemical cell, migration, mass balance, disolution rate

INTRODUCTION

Austenitic stainless steels are widely used in food raw material processing industry because have a good corrosion resistance in a very wide range of food environments [1], [2]. One of the most popular austenitic stainless alloys are chromium-nickel-iron alloys alco known as the 300 series. The AISI321 stainless steel grade has a very good corrosion behavior in a wide variety of corrosive environments, including food products, the sterilizing solutions and organic and inorganic chemicals [9]. In literature there are indications of corrosion behavior of the steel grades, but most often in pure acid solutions, the results being taken only as a guide for behavior in these environments.

Electrochemical techniques are very efficient and inexpensive tool for all investigations laboratory for studying the corrosion mechanisms. In addition to their application in basic research, electrochemical techniques are of great application in the monitoring of any change in ionic balance or migration of electrons occurring on the surface of the electrode or at the interface between the metal and the environment [4], [6]. More than that, electrochemical techniques have proven also very useful tools to study the phenomena of adsorption to the electrode surface [3]. Among the electrochemical techniques used in this field are voltammetry and potentiometry. Their widespread application is due to very good sensitivity for a very wide range of concentrations of organic and inorganic compounds, short time analysis, providing a precise relationship between the measured signal (current intensity) and concentration, all at an average cost of processing equipment.

A large number of researches are shown in the scientific literature that various methods have been applied to the study of

electrochemical phenomena in food systems interface [13], [7], [10], [8], [11].

In addition, a large number of analyzes performed to determine the electrochemical behavior of metal alloys in contact with the food used in parallel some spectrometric techniques. Thus, lately have been developed and implemented many electrochemical techniques for studying behavior under specific metals and alloys in the food industry [14].

MATERIAL AND METHODS

The aim of this research was to study by electrochemical methods the behavior of AISI321 stainless steel food grade samples in acidic corrosive environments. This paper is a continuation of the researches carried out on samples from 300 stainless steel series [12]. The aim was to increase the dissolution rate with direct effect on the limit of detection of heavy metal ions from solutions, the accuracy of measurement of the concentration of metal ions as well as productivity growth of the analytical research by reducing the time required for corrosion and diffusion.

For studying the corrosion behavior of metal samples were used discs with a diameter of 40 mm and a thickness of 2.5 mm. The sampling and sample preparation used in the experiment was made as described in the EFSA guidance note [5]. In order to avoid the contamination of the corrosive environment with foreign compounds from the surfaces of the samples materials (for removal of oil), which had been washed with a detergent solution at 40±1°C, rinsed with double distilled water at 40±1°C and then placed in the ultrasonic bath Elma H-78224 for 15 minutes. The samples were then dried in the oven at a temperature of 40±2°C.

In order to determine the surface roughness was used a *µScan* system, manufactured by *NanoFocus*. The measurement and the calculation of the commonly parameters of surfaces was carried out according to *DIN EN ISO 4287* and *DIN EN ISO 4288*. The average value of the surfaces roughness has been R_a=0.783125 µm.

To determine the chemical composition of the AISI321stainless steel samples was used LA-ICP-MS method. For this purpose has been used a laser ablation system - model UP213 (New Wave Research) coupled with mass spectrometer with inductively coupled plasma, ICP-MS - model 7500 (Agilent Technologies). The concentrations of the alloying and micro-alloyed elements of the stainless steel samples are consistent with the concentrations provided by SR EN 10088-2:2005.

The chemical compositon of the stainless steel are shown in Table 1.

Table 1 Chemical composition of the AISI321 stainless steel samples [wt %]

Fe	C	Mn	P	S	Si	Cr	Ni	Ti
68	0.08	2.0	0.045	0.03	0.75	18	11	0.4

In experimental research have been used acetic acid solutions with 3%, 6% and 9% CH3COOH in bidistilled water. The solution temperature was maintained at 22±1ºC using thermostatic bath Therm Phoenix II. The exposure time of samples for carrying out the electrochemical accelerated test was 90 min.

For conducting the accelerated electrochemical tests was used a conventional system consisting in a potentiostat-galvanostat Wenking HP 96-20 (Bank Elektronik, Germany), two multimeters Hameg HM8112-3 (Hameg, Germany) to monitor the voltage values, an original electrochemical cell and a PC system for programming, acquisition and interpretation of experimental data obtained.

As a working and counter electrode were used the AISI321 stainless steel discs. The stainless steel discs were used as working and counter electrode by mounting in the supports made of polytetrafluoroethylene (teflon) (fig. 1 a,b).
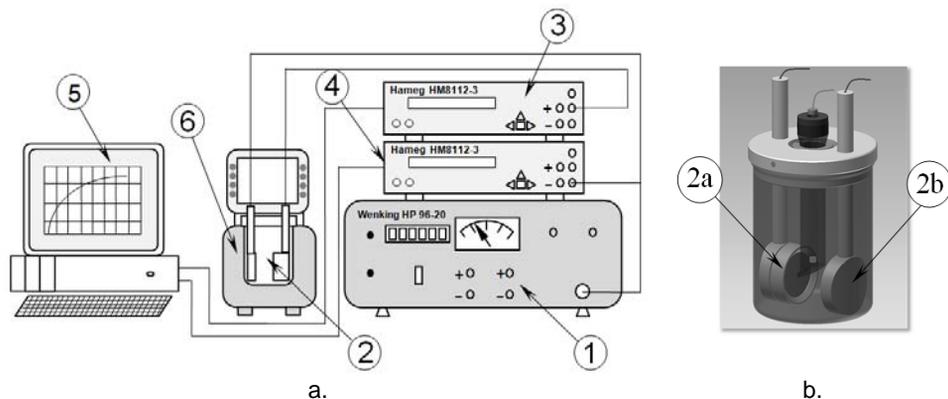
a.   b.

Figure 1a - The principle scheme of potentiostat-galvanostat system for studying the corrosion behavior of AISI321 stainless steel: 1 - potențiostat-galvanostat Wenking HP 96-20; 2 - electrochemical cell; 3 - Hameg HM8112-3 multimeter for working voltage monitoring; 4 - Hameg HM8112-3 multimeter for recording the current intensity values in the electrochemical cell; 5 - PC system; 6 - thermostatic bath

Figure 1b - Spatial view of the electrochemical cell: 2a - working electrode; 2b - counter electrode

The electrochemical cell voltages measured by the HM 8112-3 Hameg multimeter are shown in Table 2.

Table 2 Voltage in electrochemical cells

Concentration solution, [%]	3	6	9
Voltage, [V]	6.5	6.5	7.0

The metal species studied were $^{56}Fe, Mn, Cr, Ni$ and Ti. In order to develop the mass balance of the metal species migrated from AISI321 stainless steel samples in corrosive solutions the theoretically and the real balance has been calculated. To determine the theoretical masses of the metal species dissolved in acetic acid solutions was used Faraday's law (law of electrolysis) which stipulates that the mass dissolved is proportional to the amount of electricity that runs through the system. Therefore, the amount of metal dissolved from the anode is equal to the product of the gram equivalent of the metal species studied, the electric current intensity and the electrolysis time (*Relation 1*):

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

where,

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

k - gram equivalent of the species;

I - the current intensity in the electrochemical cell, [A];

t - time of electrolysis, [min.].

The value of k was calculated using the equation:

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

where,

A - atomic mass of species, [g];

z - valence of the species (Fe, Mn, Cr, Ni, Ti);

F - Faraday's constant ($F=9.648533 \times 10^4$ $C \cdot mol^{-1}$)

The values of m calculated using the Relation 1 were used to develop the theoretical mass balance. For developing of the real mass balances the acid solutions were analyzed by ICP-MS method.

In order to study the corrosion phenomenon that occurs in the electrochemical cell were calculated the dissolution rate, η (*Relation 3*):

$$\eta = \frac{m_p}{m_t} \qquad (3)$$

where,

m_p - practical masses calculated from the concentration of metal species obtained by the ICP-MS analysis, [g];

m_t - theoretical masses obtained used the Relation 1, [g];

The concentrations of electrolysis baths after 90 min. were calculated using the Relation 4:

$$C = \frac{m}{V} \rightarrow m_p = C \cdot V \qquad (4)$$

where,

C - concentration of the species analyzed by ICP-MS method, [ppb];

m_p - practical mass, [g];

V - solution volume - 300, [ml].

To calculate the theoretical mass of dissolved metal ions was used the Relation 1, using the weighted atomic mass (A_p), based on the ion concentration in the stainless steel samples (Relation 5):

$$A_p = \frac{A_{Ni} \cdot \%Ni + A_{Cr} \cdot \%Cr + A_{Fe} \cdot \%Fe + A_{Mn} \cdot \%Mn + A_{Ti} \cdot \%Ti}{5} \qquad (5)$$

RESULTS AND DISCUSSIONS

In Table 3 are shown the values of the electrolysis current evolutions in potentiostatic regime, according to the time, at various concentrations of acid food simulant environment, based on the relationship between electrolytic current and the mass of the anode metal dissolved in the electrochemical cell.

The values reflects the kinetics of anodic dissolution of metal ions from the AISI321 stainless steel samples.

Table 3 The electric current values for the AISI321 stainless steel samples in 3%, 6% and 9% acetic acid solutions

Exposure time, [*min.*]	Current value, [*A*]		
	3%	6%	9%
90	0.1290	0.1710	0.1972

In Table 4 are shown the theoretically weight values to be dissolved [*g*] for metal ions from the samples of AISI321stainless steel grade after 90 min.

Table 4 The theoretical masses as possible to be dissolved (if the dissolution rate should be 100%) for the metal ions from AISI321 stainless steel samples after 90 min., [*g*]

Chem elem. / Conc. [wt%]	Ni	Cr	^{56}Fe	Mn	Ti
3	0.03900	0.02600	0.03900	0.03900	0.01900
6	0.05200	0.03500	0.05200	0.05200	0.02600
9	0.06000	0.04000	0.06000	0.06000	0.03000

The values of dissolved real masses [*g*] of the metal ions studied and found in the simulant acid solutions (*CH₃COOH*), which have been obtained by ICP-MS spectrometer, are shown in Table 5. Thus, the dissolution rates η have been calculated by using the Relation 3.

Table 5 The real masses dissolved in acid simulant solutions from AISI321 stainless steel samples after 90 min., [*g*]

Chem elem. / Conc. [wt%]	Ni	Cr	^{56}Fe	Mn	Ti
3	0.00016	0.01414	0.00011	0.00106	0.00019
6	0.00017	0.01579	0.00014	0.00136	0.00023
9	0.00056	0.01691	0.00015	0.00159	0.00026

The values of the dissolution rates η [%] of the dissolved metal ions from AISI321 stainless steel samples in acid simulant solutions are shown in Table 6.

Table 6 The dissolution rates η of the metal ions in the 3%, 6% and 9% acetic acid simulant solutions, [%]

Chem elem. Conc. [wt%]	Ni	Cr	^{56}Fe	Mn	Ti
3	0.00424	0.53430	0.00292	0.02687	0.01002
6	0.00323	0.45011	0.00264	0.02590	0.00866
9	0.00938	0.41787	0.00263	0.02623	0.00847

By studying the values shown in Table 6 can see that the lowest dissolution rates were obtained for iron and the highest dissolution rates were obtained for the chromium.

Generally, it can be said that the dissolution rate of metal ions in acid simulant solutions decreases with increasing the concentration of CH_3COOH.

CONCLUSIONS

The experimental researches that have been carried out on AISI321stainless steel samples, under accelerated corrosion regime, using an electrical gradient overlapped a concentration gradient, as well as results obtained, have validated the validity of the method used. The dissolution rate of the metal ions in the electrochemical working regime with electrical current gradient substantially increases compared to of using the concentration gradient only.

Using the potentiostatic electrochemical technique allows the variation from almost nearly of corrosion speed and thereby also establish the optimal working conditions without achieve simulant solutions with different concentrations.

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