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CORROSION BEHAVIOUR OF STAINLESS STEEL IN CONTACT WITH WINE AND BEER

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The effects of wine and beer on the corrosion behavior of AISI 304, AISI 316 and AIS 316Ti were investigated using the electrochemical and gravimetric methods. Physical and chemical parameters of wine and beer were determined before and after the immersion of the steel plates. The corrosion behavior of materials was evaluated using the conducting cyclic potentiodynamic polarization measurements for localized corrosion. The corrosion potential (E_{corr}), and the pitting potential (E_{pit}) were determined through the application of the cyclic polarization method. Changes caused in the values of the roughness parameter *Ra* by immersing the samples into electrolytes were also studied.

Key words: corrosion, stainless steel, containers for wine and beer, cyclic potentiodynamic polarization, surface roughness

INTRODUCTION

High quality products and production economy are key factors in the whole food industry, especially in the production of wine and beer. Therefor, the crucial element for achieving high quality wines is the preservation of the organoleptic characteristics. Containers used during alcoholic fermentation are made of various materials, e.g. stainless steel, plastics and wood. Oak barrels are used for a production of specific wine sorts because of the oak’s property to impact the aromatic composition. Wood, unlike the stainless steel, is a porous material which can interact with various wine compounds. Several studies have described the influence of wood compounds on the aroma of white wine (Pérez-Coello et al., 2000 [1], Chatonnet et al., 1991 and Herjavec et al., 2007). However, few studies exist that show the influence that the type of container has on the fermentation bouquet of wine. Yokotsuka, Matsunaga, and Singleton (1994) compared the composition of Koshu white wines fermented in oak barrels and to those fermented in plastic tanks and found a larger formation of esters, especially ethyl acetate, in wines fermented in oak barrels. If wine is stored for a long period of time in oak barrels, it will come in contact with the oxygen from the air through oak filter. This will lead to the loss of freshness. It is also important to note that the rate of oak tree growth is insufficient to keep up with the ever-increasing demand. Therefore there is now a need for new materials that can be used in the construction of wine containers, such as polymer materials reinforced with glass wool or concrete, on the other hand.

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The use of stainless steel tanks for fermentation and wine storage began in the 1950s in the USA and approximately three decades later in Chile and Argentina. The main advantages of stainless steel tanks over tanks made of other materials are: (i) ease of cleaning; (ii) relative chemical inertness, e.g. no addition of flavors or contaminants; (iii) improved control of the fermentation process; and (iv) esthetically appealing appearance. However numerous studies have shown that even such wine containers cannot preserve wine for longer periods of time, which can be seen by the changes in the organoleptic characteristics of wines. We can assume that the causes of these changes are changes in the composition of wines themselves. These changes can occur due to the elution of metal ions from the metal walls of the containers into wine or beer [2-7]. The quality of a particular wine is determined by its, roughly, eight hundred components. It can be expected that change of the percentage of any one of these components in wine, as well as change in the structure of the components themselves can affect the quality of wine. For these reasons, the existence of electrochemical cell on the surface of the sheet metal can be dangerous for the long term preservation of wine, due to the fact that the share of certain components in wine is being reduced, while that of others is being increased, especially that of iron (Fe^{2+}) ions. All of these occurrences affect the quality of wine, which is an unwanted situation in a storage unit. The assertion that the existence of electrochemical cell affects the organoleptic properties of wine is corroborated by the fact that if the barrels are welded together by a material of a different composition than that of plate there is a faster change in the organoleptic characteristics of wine. This is due to the fact that the differences of electropotential on the surface, where wine comes in contact with the plate, are now greater [7-11]. The electrochemical cell on steel-wine phases can be seen in the following reactions:

$$Me \rightarrow Me^{z+} + ze^{-} \quad (1)$$

(anodic reaction; metal dissolution, oxidation)

$$e.g. Fe \rightarrow Fe^{2+} + 2e^{-} \quad (2)$$

$$R_1C = CR_2 + 2e^{-} + 2H - g\ R_1HC - CHR_2 \quad (3)$$

(R_1, R_2 – radicals bound to carbon atoms, cathodic reaction, consume the electrons, reduction)

EXPERIMENTAL PROCEDURE

This paper examines the behavior of high alloy steels, which are used in the production of wine and beer containers as well as their effects on the organoleptic characteristics of wine. The containers mentioned in this article are made using the electrochemical and gravimetric methods.

Corrosion behavior of the stainless steel was observed in beer, red and white wines. Test were carried out on the dry red wine from the "Babic" grape sort from Sibenik vineyards on the white wine "Riesling" from Krapina vineyards, and on the "Ozujsko" light beer. The electrochemical corrosion behavior of materials AISI 304, 316 and 316Ti was evaluated using the conducting cyclic potentiodynamic polarization measurements for localized corrosion susceptibility (pitting and crevice corrosion) test method which is similar to the one described in ASTM G61. The corrosion parameters of the stainless steel materials were obtained using the Potentiostat/Galvanostat device, more specifically Versa STAT 3 (Ametek) model. In these tests a standard electrochemical reactor was used together with a graphite counter electrode and a reference saturated calomel electrode (+ 0,2414 mV) which was itself in contact with a working electrode. The capacity of the polarization cell used was 1 000 mL. Austenitic stainless steels with an exposed area of 1 cm^2 were used. The electrode was polished with the emery paper 600 and then washed in distilled water and degreased in ethyl alcohol before use. Potentiodynamic polarization tests were carried out with red and white wine, as well as beer at a temperature range of 22 °C ± 2 °C. The cyclic polarization test was performed by recording polarization curves in the area of potential from the corrosion potential and the rate of potential change of 0,5 mVs^{-1}. The corrosion potential (E_{corr}), and the pitting potential (E_{pit}) were determined through the application of the cyclic polarization method. Using the gravimetric method i.e. through weighing the stainless steel plates with dimensions 50 mm x 25 mm x 1 mm before and after they were immersed in 250 ml electrolyte (wine and beer), we have determined the mass reduction that occurred during their fourteen-day exposure period. Physical and chemical parameters of wine and beer were determined before and after the immersion of the steel plates, and are shown in the Table 1. Conductivity, total dissolved soils, salinity, resistivity and pH in wine, water and beer were also investigated with pH /Conductivity Mettler Toledo. The InLab 413 pH glass indicator electrode (pair glass / saturated calomel electrode) was used to measure the pH value, and the InLab 730 electrochemical cell was used to measure electrical conductivity, salinity and total dissolved solids (TDS).

The method of Atomic Absorption Spectrophotometrics (AAS) was used to determine the levels of Cr, Ni and Fe in beer and wine before and after immersion of steel plates. These measurements were conducted on the Pye unicam SP9 atomic absorption spectrophotometer.

A change in the roughness parameter *R*a was noticed in all samples, the cause of which was the exposure of the samples to the electrolyte. The surface roughness parameter *Ra* was measured using the stylus S8P instrument with the *ln* evaluation length being set at 4 mm and the shortwave Gaussian filter with the cut-off λc wavelength being set at 0,8 mm. The surface topography of the steel AISI 304 after the immersion in the red wine was observed with a scanning electron microscope SEM Tescan. The results of surface topography analysis are shown in the Figure 1.

RESULTS AND DISCUSSION

One of the technologies for improving the wine quality is micro-oxygenation. Micro-oxygenation is carried out spontaneously in wooden barrels. However, in stainless steel tanks the pure oxygen must be introduced through ceramic membranes at the tank bottom. Oxygen addition must be monitored and controlled since oxygen surplus can lead to negative effects, i.e. astringency wine, phenol oxidation and affect microorganism levels. *P* and *n* types oxides are created on the metal surface of the stainless steel depending on the oxygen concentration. *N*-type oxides are more susceptible to pitting corrosion. Different electrochemical potentials of *n* and *p* types of oxides in contact with wine and beer cause electrochemical processes.

Salas et al. [3] explain the phenomenon of the stainless steel corrosion in wine due to the SO_2 presence i.e., bisulphate ion (HSO_3^-) and citric, tartaric, tannic, acetic and malic acids which also have corrosive influence on stainless steels. Table 1 shows the values of pH, conductivity, total dissolved soils, salinity and concentration of metallic ions in red and white wine and beer, before and after the exposure of the stainless steel plates to it.

Table 2 shows the mass reduction as well as the change in the values of the *R*a roughness parameter caused by immersing the samples into the electrolytes.

The corrosion parameters E_{corr} and E_{pit} which are determined by applying the cyclic polarization method are given in Table 3.

An SEM image of AISI 304 after testing in red wine is shown in Figure 1 which shows the dissolution of metallic ions from the surface.

Table 1 **The physical and chemical properties of the electrolytes before and after the fourteen-day immersion of the metal plates**

		Beer	White wine	Red wine
Before	pH / unit	4,165	2,956	3,320
	Cond./ µS/cm	1 564	1 360	1 458
	TDS / mgL^{-1}	781	681	728
	SAL / ‰	0,74	0,64	0,69
	Ni / %	-	-	-
	Cr / %	-	-	-
	Fe / %	-	-	-
After AISI 304	pH / unit	3,362	2,876	2,905
	Cond. / µS/cm	2 350	2 150	2 750
	TDS / mgL^{-1}	1 174	1 076	1 375
	SAL / ‰	1,18	1,07	1,40
	Ni / mgL^{-1}	0,05	0,07	0,03
	Cr / mgL^{-1}	-	-	-
	Fe / mgL^{-1}	0,35	1,00	1,2
After AISI 316	Ph / unit	3,359	2,874	2,909
	Cond. / µS/cm	2 360	2 130	2 700
	TDS / mgL^{-1}	1 183	1 063	1 352
	SAL / ‰	1,19	1,05	1,37
	Ni / mgL^{-1}	0,02	0,01	0,01
	Cr / mgL^{-1}	-	-	-
	Fe / mgL^{-1}	0,15	0,95	0,85
After AISI 316Ti	pH / unit	3,348	2,876	2,905
	Cond. / µS/cm	2 350	2 160	2 760
	TDS / mgL^{-1}	1 173	1 078	1 381
	SAL / ‰	1,18	1,07	1,40
	Ni / mgL^{-1}	0,01	0,02	0,01
	Cr / mgL^{-1}	-	-	-
	Fe / mgL^{-1}	0,07	0,10	0,09

Table 2 **The gravimetrically determined loss of mass and roughness parameter after the fourteen-day exposure period**

		Beer	White wine	Red wine
AISI 304	Δ*m* / g	0,0016	0,0015	0,0010
	Δ*Ra* / µm	0,0150	-0,0010	0,0110
AISI 316	Δ*m* / g	0,0011	0,0011	0,0021
	Δ*Ra* / µm	0,0190	0,0170	0,0200
AISI 316Ti	Δ*m* / g	0,0130	0,0010	0,0004
	Δ*Ra* / µm	- 0,0020	- 0,0290	- 0,0200

Table 3 **The results of cyclic polarization**

Material		Beer	White wine	Red wine
AISI 304	E_{corr} vs SCE / mV	- 390	- 380	- 390
	E_{pit} vs SCE / mV	400	900	1 180
	Area hysteresis loop / mC	83,52	-	-
AISI 316	E_{corr} vs SCE / mV	- 450	- 380	- 405
	E_{pit} vs SCE (mV)	1 000	905	1 350
	Area hysteresis loop / mC	86,36	-	-
AISI 316Ti	$E_{corr,}$ vs SCE / mV	- 400	- 382	- 410
	$E_{pit,}$vs SCE /mV	950	907	1 350
	Area hysteresis loop / mC	222,3	-	-

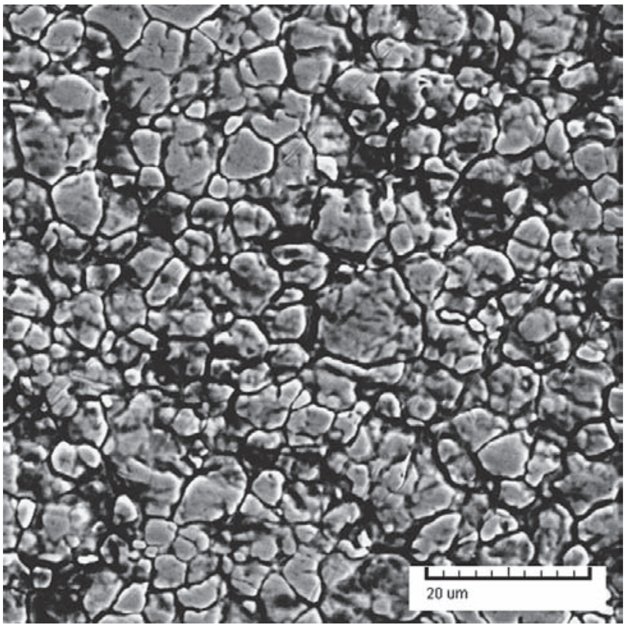

Figure 1 SEM micrograph of the AISI 304 after fourteen-day exposure in red wine

CONCLUSIONS

Based on the research that was carried out, the following conclusions have been reached:

The largest loss of mass was exhibited by sample AISI 316 L, after it was exposed to beer. The strongest deviation in terms of roughness was measured in sample AISI 316, after it was exposed to red wine. The highest susceptibility towards pitting corrosion is exhibited by the steel in the AISI 316Ti sample, after it was exposed to beer. Wine containers can be constructed from stainless steel sheet metal. The storage of wine in this kind of containers for a prolonged period of time is not recommended. The dissolution of the stainless steel wall, which comes in contact with the wine, can be caused by electrochemical processes which occur on the border between the phase of the metal and the wine. It can furthermore be assumed that these electrochemical processes occur due to the differences in electric potential, or in other words, due to the micro electrochemical cell located on the surface of the metal, which, in turn, resulted from the destruction of the passive film, Cr_2O_3. This then causes certain organic components of wine to change. The effect of surface roughness on the elution of molybdenum and titanium in the austenitic stainless steels will be examined in further research.

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