Influence of gamma irradiation on thin film surface coating of copper

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INTRODUCTION

Copper is a reddish-gold metal that is easily worked and drawn, it conducts both heat and electricity very well. Because of its very good properties it has a wide range of applications and is exposed to various often aggressive environments. Therefore, additional protection is required to enhance the protective properties of its naturally formed oxide film.

Formation of a thin protective film on the copper surface is a good and practical way to enhance the metal's natural protective properties. Fatty acids are non-toxic compounds which have an affinity for adsorbing on metals with their hydrophobic end, the carboxyl group. The other end of fatty acids, the methyl group, has hydrophobic properties and when adsorbed on the metal surface it makes the whole surface of the metal appear hydrophobic. Thus by blocking access for water to the surface the dissolution of the metal is disabled. Elaidic acid is a monounsaturated fatty acid found in hydrogenated vegetable oils. Because of its specific shape that it has thanks to the trans form of the double bond its molecules are close-packed on the surface of copper (Fig. 1) making the coating very compact and water difficult to approach the surface.

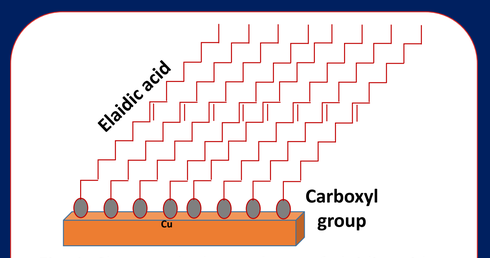


Fig. 1. Close-packed monolayer of elaidic acid on the surface of copper.

EXPERIMENTAL

Electrode: Cu (99.9%)
Counter electrode: Pt electrode
Reference electrode: SCE
Electrolyte: 3 % NaCl
Inhibitor: Elaidic acid (EA), $CH_3(CH_2)_7CHCH(CH_2)_7CO_2H$ dissolved in ethanol at c = 0.001 mol/L
Preparation of treated samples:

- Copper samples heated in furnace for 4h at 75 °C
- Immersed in SA/EtOH for 18h at 40 °C
- Drying in air at room temperature
- Gamma irradiated in air with 0.1, 1, 3, 5, 7, 10 kGy at 31 kGy/h (8.6 Gy/s)

Determination of the optimal irradiation dose

Table 1. Corrosion parameters obtained from the polarization curves

	D, kGy	E_{corr}, mV	b_a, mV dec^{-1}	$-b_c$, mV dec^{-1}	j_{corr}, µA/cm^2
-	-	-236	76	240	5.470
Elaidic acid (EA)	0	-215	46	137	2.811
	0.1	-222	45	104	2.682
	0.5	-222	41	101	1.703
	1	-202	30	105	1.684
	3	-211	38	104	1.514
	5	-215	41	124	1.709
	7	-206	37	119	2.593
	10	-208	44	132	3.054

- A potential shift in the more noble direction, i.e. towards more positive potentials when EA is present on the surface
- The lowest currents are observed on samples irradiated after EA adsorption
- The lowest j_{corr} is observed on the sample irradiated with 3 kGy.
- Presence of EA on the surface decreases both Tafel slopes b_a and b_c indicating that both processes progress slower when EA is present on the surface. This would mean that EA behaves as a mixed inhibitor.

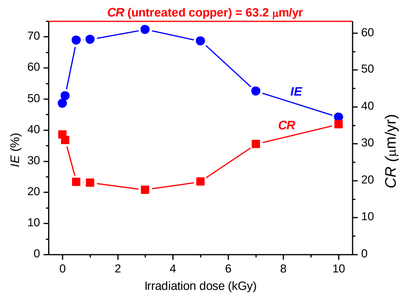


Fig. 2. Inhibitor efficiency and corrosion rates calculated from the wide range polarization curves.

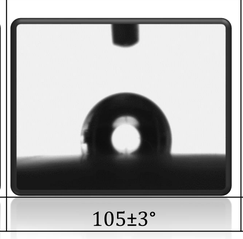
$$IE = \frac{j^0_{corr} - j_{corr}}{j^0_{corr}} * 100\%$$

IE [%] – inhibitor efficiency
j^0_{corr} [µA/cm^2] – corrosion current density of non-treated copper
j_{corr} [µA/cm^2] – corrosion current density of copper treated with EA

$$CR = \frac{M}{nF\rho} j_{corr}$$

CR [µm/yr] – corrosion rate
M = 63.55 g/mol – molar mass of copper
n – number of electrons transferred
F = 96 485 C/mol – Faraday's constant
ρ = 8.96 g/cm^3 – copper density

Table 2. Contact angles of a drop of water on different copper samples

Pure copper	EA + 0 kGy	EA + 3 kGy
		
69±5°	105±3°	128±2°

- EA's presence leads to a large increase in the contact angle, i.e. the surface becomes significantly more hydrophobic. The hydrophobic properties of the surface play an important role in corrosion inhibition since when H_2O is not present on the surface of a metal it will not corrode. Non-polar interactions between the long alkyl chains of the molecules due to van der Waals forces also are responsible for protective quality of the film.
- The contact angle is even greater after irradiation (128°) which indicates that the alterations that gamma irradiation induced on the surface layer have resulted in making the film even more hydrophobic.

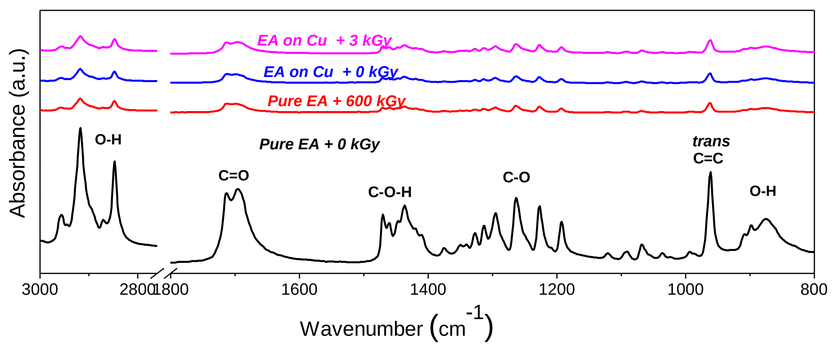


Fig. 3. FTIR analysis obtained on the different copper samples

- There is no significant difference between the bands of the irradiated and unirradiated samples indicating that irradiation does not change the adsorbed molecules in the investigated dose range but rather influences the adsorption and ordering itself.
- Since FTIR spectra characteristic for EA were obtained on the samples where EA is adsorbed on the surface of copper, and knowing that the penetration depth of FTIR-ATR is not less than 1 mm, it is clear that a multilayer of molecules is present on the surface rather than a monolayer.
- Since the same peaks were observed on pure EA that was irradiated with 600 kGy it is obvious that this fatty acid is very stable under the influence of gamma irradiation.

Establishing reaction mechanisms

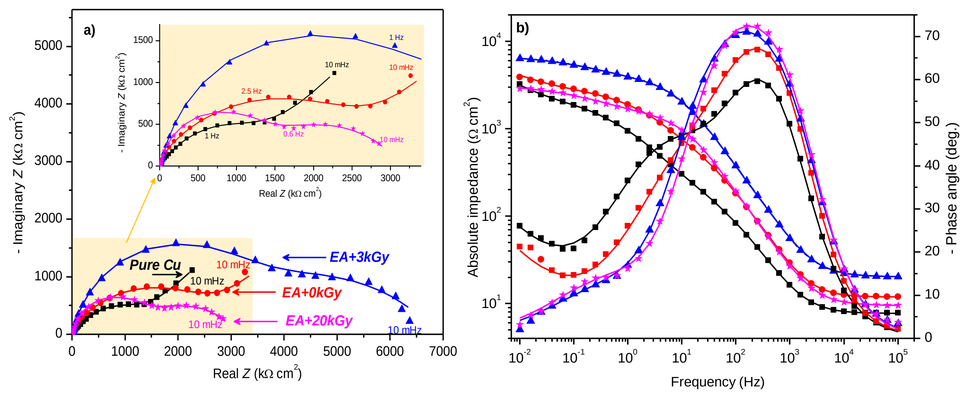
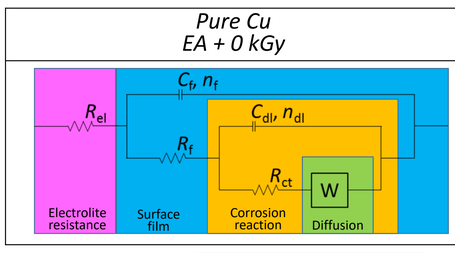
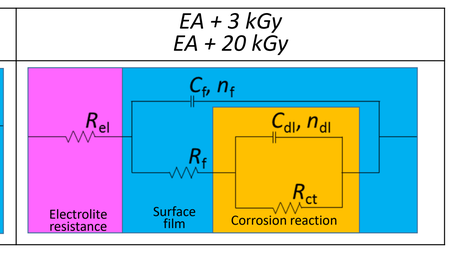


Fig. 5. (a) Nyquist and (b) Bode plots presenting the EIS data obtained on different copper samples in 3 % NaCl

- The sample that was treated with EA and irradiated has the largest capacitive loop (Fig. 5a), i.e. the largest absolute impedance in the whole frequency range (Fig. 5b).
- Unprotected copper with only a naturally occurring oxide layer on the surface shows the lowest $|Z|$ (Fig. 5b).
- Experimental EIS data exhibits two time constants under the capacitive loop in the case of all samples, although they are not well separated. The electrochemical process involves therefore one reaction intermediate in addition to the contribution of the double layer capacitance.

Table 3. Equivalent electrical circuits used for fitting the EIS data

Pure Cu EA + 0 kGy	EA + 3 kGy EA + 20 kGy
	

R_{el}, R_{ct}, R_f - electrolyte, charge transfer and surface film resistances respectfully (W cm^2)
C_{dl}, C_f – double layer and surface film capacitances respectfully (F/cm^2)
n_{dl}, n_f – coefficients represent the depressed feature of the R-C circuits respectfully
W – Warburg impedance

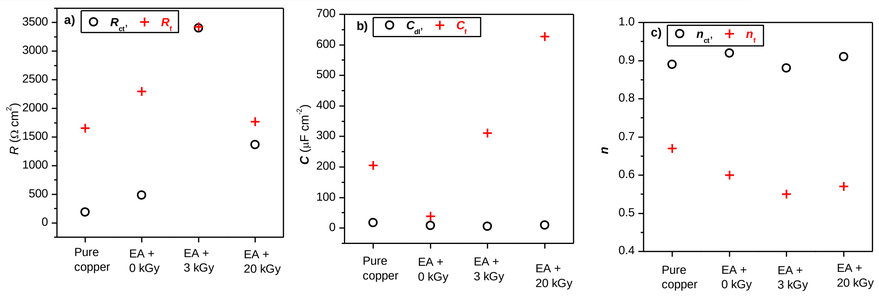


Fig. 6. Results of the regression calculation of the EIS data using the equivalent electrical circuits presented in Table 3.

- For the regression calculation of the EIS data two equivalent electrical circuits were used (Table 3). The circuits consist of the electrolyte resistance, (R_{el}) coupled with the R_{ct}-C_{dl} circuit representing the corrosion reaction at the metal substrate/solution interface and the R_f-C_f circuit representing the film that covers the surface of copper. In the cases where diffusion occurs in the corrosion reactions it creates impedance known as the Warburg impedance (W).
- Diffusion (W) of soluble $CuCl_2^-$ from outer Helmholtz plane into the bulk solution [22] occurs in the case of untreated copper, but also on the unirradiated EA coated sample where the film is still diffuse.
- Both R_{ct} and R_f have the smallest values in case of untreated copper, while they increase when EA is present on the surface.
- The curves in Fig. 5 representing irradiated samples clearly have a different shape compared to the unirradiated samples. On these samples diffusion was not observed.
- Irradiation does not influence markedly the C_{dl} which indicates that the EA film uniformly covers the surface of copper, i.e. oxide film.
- The sample that was irradiated with 3 kGy obtained the largest values of all samples for both Rct and Rf.
- R_{ct} increases after irradiation 18 times for the sample irradiated with 3 kGy compared to untreated copper. This resistance is mainly determined by the redox process of Cu(0)↔Cu(I), so the increase in resistance indicates that presence of EA on the surface decreases markedly the electrochemical reactivity of bronze, which is reflected in the decrease of the exchange current density in Table 1 (from 5.470 to 1.514 µA/cm^2).
- C_f decreases when EA is applied on the surface and not irradiated indicating an efficient inhibitive effect towards the redox process taking place at the electrode surface when coupled with an increase in R_f.
- C_f and R_f increase after irradiation indicating that the film got thinner probably because of stronger adsorption, and as a result better ordering of molecules on the surface of the oxide film, i.e. the film is more compact and offers stronger protection towards corrosion by blocking the surface towards O_2 and H_2O molecules. This is confirmed by absence of the Warburg element, which indicates that the electrochemical process is not controlled by diffusion through the film.

CONCLUSIONS

- The influence of gamma irradiation on a fatty acid self-assembled molecular layer (SAM) formed on copper by elaidic acid (EA) has been investigated.
- It has been established that gamma irradiation further improves the properties of the EA nanocoating. Irradiation at doses from 0.5 to 5 kGy enhance significantly the protective properties of the EA surface layer, while the best properties were obtained when irradiated with 3 kGy, where the inhibitor efficiency was 72 %.
- Both cathodic and anodic processes progress slower when EA is present on the surface. This would mean that EA behaves as a mixed inhibitor.
- Presence of EA on the surface increases copper's hydrophobic properties significantly, and this increase is even greater after irradiation.
- The results have shown that a multilayer of molecules is present on the surface rather than a monolayer. The results have also shown that EA is very stable under the influence of gamma irradiation.
- The EIS results have shown that the surface film got thinner probably because of stronger adsorption, and as a result better ordering of molecules on the surface of the oxide film. The film after irradiation is more compact, as only after irradiation diffusion through the film was not observed, indicating that the film blocks the surface.