Hrana u zdravlju i bolesti, znanstveno-stručni časopis za nutricionizam i dijetetiku (2018) 7 (1) 6-11
Food in Health and Disease, scientific-professional journal of nutrition and dietetics (2018) 7 (1) 6-11

INHIBITION OF ALUMINIUM ALLOY CORROSION IN CHLORIDE SOLUTION BY CAFFEINE ISOLATED FROM BLACK TEA

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original scientific paper

Summary

Caffeine (1,3,7-trimethylxanthine) was isolated from black tea and characterised using different physical methods. The corrosion inhibition performance of the caffeine isolate (in concentration from 1×10^{-5} to 1×10^{-3} mol/dm^3) on aluminium alloy corrosion in neutral 0.5 mol/dm^3 NaCl solution was investigated using potentiodynamic and linear polarization measurements at 20 °C. Corrosion potential, corrosion current and polarization resistance were determined and surface coverage of inhibitor molecules and inhibition efficiency were calculated. The obtained results show that caffeine effectively inhibited the corrosion reaction in the chloride solution with an inhibition efficiency of up to ≈ 76%. Furthermore, caffeine was found to function essentially as a mixed type with a higher influence on cathodic reaction. The adsorption behaviour of investigated inhibitor can be described by the Freundlich adsorption isotherm. The adsorption free energy closes to -10 kJ/mol indicates physical adsorption of the caffeine on the aluminium alloy surface in NaCl solution.

Keywords: aluminium alloy, corrosion, inhibition, caffeine

Introduction

The unique combinations of properties provided by aluminium and its alloys make aluminium one of the most versatile, economical, and attractive metallic materials for a broad range of uses from soft, highly ductile wrapping foil to the most demanding engineering applications. Aluminium alloys are in the second position in use as structural metals just behind the steels (Davis, 2001). The resistance of aluminium and its alloys against corrosion has been attributed to a rapidly formed surface oxide film. The major corrosion problem is the localised breakdown of the passive film in the presence of chloride ions, which leads to the initiation and growth of corrosion pits.

One of the common methods for the corrosion protection of aluminium is the use of organic inhibitors; however, widespread application of many commercial organic inhibitors has been hindered by cost and toxicity considerations. Accordingly, several studies have focussed on identifying effective, inexpensive and nontoxic alternatives. Some of such investigations have assessed the corrosion-inhibiting properties of natural products of plant origin, which have been found to generally exhibit good inhibition efficiencies (El-Etre et al., 2005; Raja, Sethuraman, 2008; Sengeetha et al., 2011). This area of research is significant because plant products are inexpensive, readily available and renewable sources of environmentally acceptable materials. This paper focuses on aluminium alloy corrosion inhibition in NaCl using caffeine (1,3,7-trimethylxanthine) isolated from black tea.

Black tea is usually obtained from the Assamese plant (*Camellia sinensis* subsp. *assamica*) and is additionally fermented, hence more oxidized and stronger in flavour than green or white tea (Finger et al., 1992; Fernández et al., 2000). Caffeine (Fig. 1) belongs to a class of methylxanthine alkaloids present in coffee, cocoa beans, cola nuts and tea leaves (Mumin et al., 2006). Caffeine is extensively used in the production of non-alcoholic beverages and pharmaceuticals because of its stimulating and muscle relaxing properties. Accordingly, the effect of caffeine on human health and behaviour has been relatively well documented (Smith, 2002; Glade, 2010). Studies on the adsorption and protective effect of commercially available caffeine on the corrosion of various metals and alloys in different aggressive solutions have shown that this organic compound has a considerable corrosion-inhibiting potential and, thus, deserves more in-depth investigation (Fallavena et al., 2006; Trindade, Goncalves, 2009; Gudić et al., 2014). Again, in line with current efforts at promoting the utilization of biomass resources for the reasons mentioned earlier, it is also necessary to similarly assess the corrosion-inhibiting efficacy of caffeine isolated from biomass extracts.

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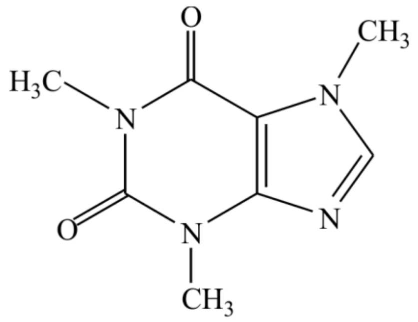

Fig. 1. Structural formula of caffeine

The present study evaluates the corrosion inhibition performance of caffeine isolated directly from black tea on AA 2017A aluminium alloy in neutral NaCl solution using potentiodynamic and linear polarization measurements.

Materials and methods

Materials preparation

The working electrode was made from AA 2017A aluminium alloy, which chemical composition was shown in Table 1. The electrical contact for the electrochemical measurements was achieved by soldering the aluminium alloy with the copper wire and then isolated them with acrylic resin leaving only one side exposed to the electrolyte.

Prior to electrochemical measurements the electrode surface (0.5 cm^2) was mechanically treated by grinding with different emery papers and polishing to a mirror finish, followed by the alkali pickling in 0.1 mol/dm^3 NaOH (T = 40 °C) for 1 min. The electrode was then rinsed in doubly distilled water. A new electrode surface was used for each run.

Table 1. Chemical composition of investigated AA 2017A aluminium alloy

element	wt. %	element	wt. %
Si	0.67709	Ni	0.00305
Fe	0.62080	Pb	0.02014
Cu	4.35373	Sn	0.00136
Mn	0.91555	Bi	0.00238
Mg	0.68498	Zr	0.12424
Zn	0.05766	Be	0.00014
Ti	0.03892	Al	92.4876
Cr	0.01238		

Isolation and characterization of caffeine

Caffeine isolation from black tea and its characterisation using different physical methods (including determination of melting point, thin layer chromatography, UV and Fourier transform infrared spectroscopy) are described in detail in previous work (Gudić et al., 2014). From the amount of 30 g of black tea (Franck, Zagreb, Croatia) 0.4332 g of caffeine was obtained.

The melting temperature was determined by differential scanning calorimetry (DSC) using a Differential Scanning Calorimeter (Mettler Toledo 823E). Thin layer chromatography (TLC) was performed on a commercial aluminium plate 20 × 20 cm coated with a 0.2-mm thin layer of silica gel and the crystalline caffeine using a 9.5:0.5, v:v mixture of chloroform and ethanol as mobile phase and visualized under a UV-lamp (λ = 254 nm). The UV-absorption spectrum of the extracted crystalline caffeine was obtained using a UV/VIS spectrophotometer (PerkinElmer Lambda EZ 201). The Fourier transform infrared (FTIR) spectrum of isolated caffeine was recorded on a Perkin Elmer FTIR spectrophotometer (Spectrum One) over a wave number range of 4000 – 650 cm^{-1} with a resolution of 4 cm^{-1} (Gudić et al., 2014).

Corrosion measurements

Electrochemical measurements were performed in a conventional three-electrode glass cell (equipped with saturated calomel electrode (SCE) as reference and platinum sheet as a counter electrode) using a potentiostat/galvanostat (PAR M273A) connected with personal computer. Measurements were performed in deaerated and stagnant 0.5 mol/dm^3 NaCl solutions at 20 ± 1 °C in which caffeine was added in concentrations from 1×10^{-5} to 1×10^{-3} mol/dm^3. Potentiodynamic current-potential curves were obtained by changing the electrode potential from –250 to +250 mV versus the open circuit potential, E_{OC}, with a scan rate of 0.5 mV/s. The polarization resistance, R_p, was determined from the slope of polarization curves obtained by measurements in the potential range ± 20 mV vs. E_{OC}, with scan rate of 0.2 mV/s.

Results and discussion

Characterization of caffeine

The analysis of the crystalline material isolated from black tea using the DSC, TLC, UV and FTIR spectroscopy confirmed the presence of high purity caffeine.

The thermal behaviour of caffeine is presented in the DSC thermogram shown in Fig. 2 and reveals a sharp endothermic peak at 235 °C (Gudić et al., 2014).

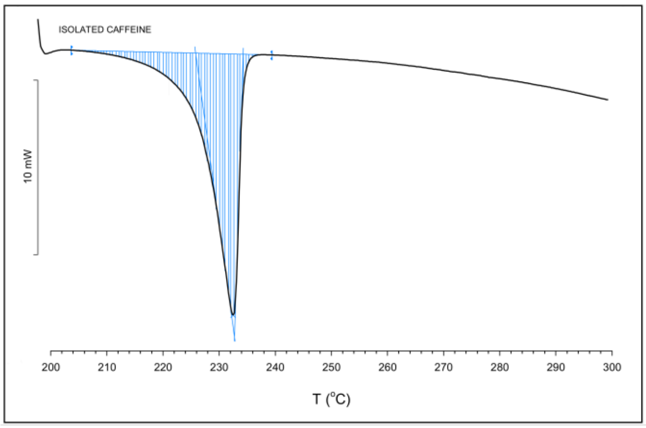

Fig. 2. DSC curve of caffeine isolated from black tea (Gudić et al., 2014)

For the TLC experiment, the plate, after evaporation of the solvent, was visualized under UV light (with $\lambda = 254$ nm) and revealed one brown spot. The R_f value of the isolated caffeine was found to be 0.63, which is consistent with the published data, and is very close to the R_f value of the reference sample of commercial caffeine (0.64) (Mumin et al., 2006). The characteristic UV absorption spectrum and absorption maximum (λ_{max}) were also employed in identification of the isolated compound. The λ_{max} was 272.9 nm for the isolate in water as solvent and 272.6 nm in ethanol as solvent, which is similar to the values reported in the literature for caffeine (Mumin et al., 2006). The λ_{max} values of the isolate also coincide with the values of the reference samples (commercial caffeine).

The FTIR spectrum of the isolated caffeine showed comparable absorption bands with that of standard caffeine (Fig. 3). The bands due to aromatic C-H stretching appear at 3112 cm^{-1} (correspond to C-H) and 2954 cm^{-1} (corresponds to C=H). The C=O stretching frequency appears at 1701 cm^{-1}. The band at 1658 cm^{-1} is due to C=C stretching. The band at 1239 cm^{-1} is attributed to C-N, while that at 1549 cm^{-1} is assigned to C=N (Gudić et al., 2014). The match between the spectra of the isolated caffeine and spectra from the base data was 97.2%. The above findings all point towards the purity of the caffeine as isolated from black tea.

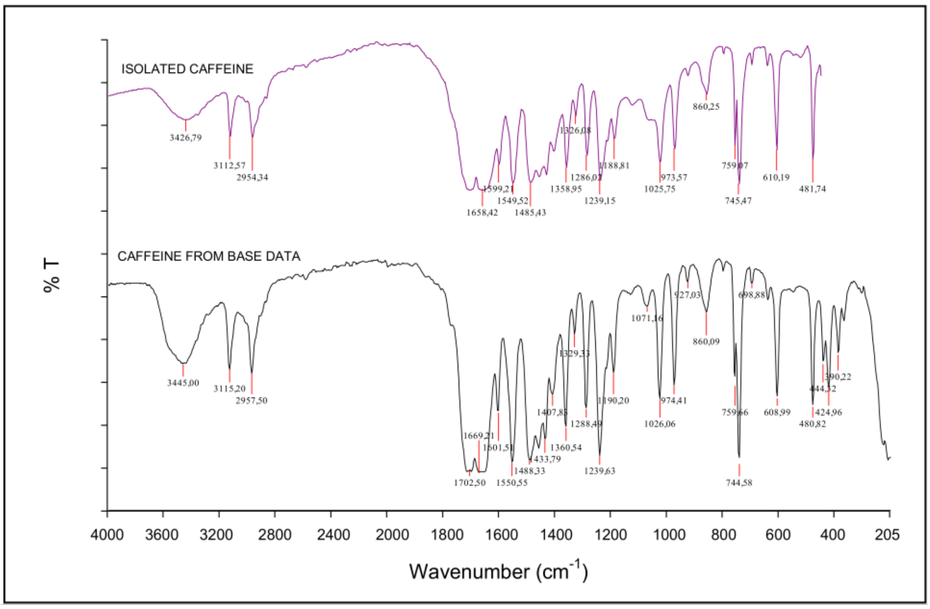

Fig. 3. FTIR spectra of caffeine isolated from black tea and caffeine from base data of instrument (Gudić et al., 2014)

Potentiodynamic polarization measurements

The nature of the corrosion inhibition process may be determined on the basis of polarization measurements. Thus, changes in the polarization curves after the addition of inhibitors typically are used as criteria for classification an inhibitor as cathodic, anodic or mixed type. Typical potentiodynamic polarization curves for AA 2017A aluminium alloy in NaCl solution in the absence and presence of the lowest and highest concentration of caffeine are shown in Fig. 4.

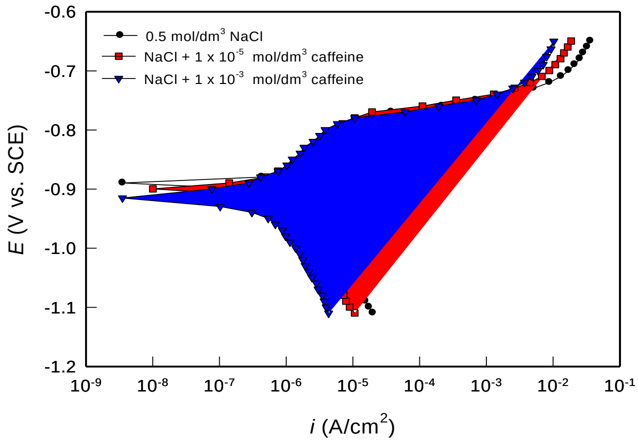

Fig. 4. Potentiodynamic polarization curves for AA 2017A alloy in NaCl solution in the absence and presence of lowest and highest concentration of caffeine

On the polarization curve for Al alloy in NaCl solution, a tight passive area is observed just above the corrosion potential in the potential range from ≈ -0.98 V to ≈ -0.80 V. In this potential area growth of the oxide layer takes place on the alloy surface. Anodic current slowly rises until a so-called breakdown potential is reached (≈ -0.77 V). Above breakdown potential a passive layer breakdown takes place due to the pitting corrosion and anodic current rises sharply. As the solution was deaerated by purging with argon, a cathodic part of the polarization curves probably represent hydrogen evolution reaction.

The presence of caffeine causes significant changes in the polarization behaviour of the Al alloy. The reduction of the anodic and cathodic current density along with the slight changes the values of corrosion potential in the cathodic side can be observed. Decreasing the cathodic current density along with the changes of corrosion potential in cathodic direction are characteristic of cathodic corrosion inhibitors, while decreasing the anodic current density along with the changes of corrosion potential in positive direction is characteristic of anodic corrosion inhibitors. Mixed inhibitors act by reducing both the cathodic and anodic current densities without any significant changes of corrosion potential values. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to corrosion potential in the absence of the inhibitor (Tao et al., 2009).

According to the observed changes in polarization behaviour of AA 2017A alloy, it could be said that caffeine belongs to a mixed type of inhibitor, with increased influence on cathodic reaction. Table 2 shows the electrochemical polarization parameters for AA 2017A alloy in NaCl solution in the presence and absence of coffeine. The parameters include the corrosion potential (E_{corr}), corrosion current density (i_{corr}), as well as inhibition efficiency (η) which were determined using the relation (1):

$$\eta = \frac{i_{corr} - (i_{corr})_{inh}}{i_{corr}} \times 100 \qquad (1)$$

where i_{corr} and $(i_{corr})_{inh}$ represent corrosion current in the absence and presence of inhibitor.

Inhibitor action can be explained by simple adsorption on the electrode surface and by blocking active sites on the surface, which leads to a reduction of corrosion. In general, the adsorption processes in the metal/solution interface resulting in separation of the solute in solution (inhibitor), and its concentration on the metal surface. This process takes place until the establishment of the dynamic equilibrium between the concentration of the residual solute in the solution and its concentration on the metal surface. Thus, in the adsorption process metal surface is covering with inhibitor which slows down the corrosion of metal. According to the Table 2 it can be seen that the inhibition efficiency increased with caffeine concentration.

Table 2. Corrosion parameters for AA 2017A aluminium alloy in 0.5 mol/dm^3 NaCl solution in the absence and presence of caffeine

$c_{caffeine}$ (mol/dm^3)	E_{corr} (mV)	i_{corr} (μA/cm^2)	η (%)
0	-889.0	1.44	
1×10^{-5}	-899.5	0.64	55.90
1×10^{-3}	-915.0	0.35	75.98

Linear polarization method measurements

By linear polarization method (polarization resistance determination method), the influence of caffeine on the inhibition of corrosion of AA 2017A alloys in NaCl solution was investigated in detail. Fig. 5 shows the linear parts of the polarization curves for the alloy in all tested solutions. The addition of caffeine changes the slope of the linear part of polarization curves, i.e. lead to a rise of curve slopes. The polarization resistance (R_p) can be defined by equation:

$$R_p = \frac{\Delta E}{\Delta i} \qquad (2)$$

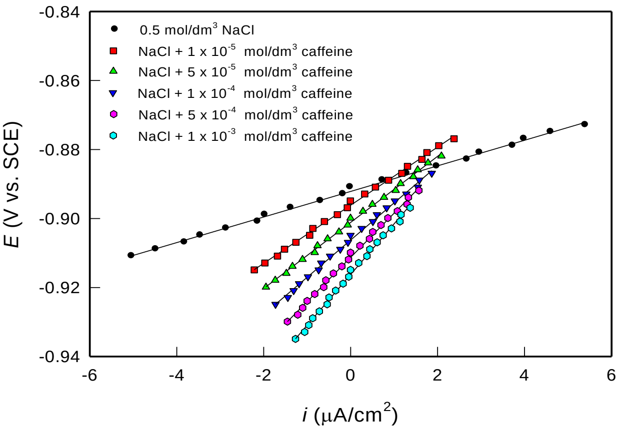

Fig. 5. Linear polarization curves for polarization resistance determination of AA 2017A alloy in NaCl solution in the absence and presence different concentration of caffeine

Thus, increasing the slope of the linear part of polarization curve indicates an increase in the value of polarization resistance. Since the electrochemical theory assumes that $1/R_\mathrm{p}$ is directly proportional to the corrosion rate, the surface coverage (θ) and inhibition efficiency (η) was calculated according to equation 3:

$$\eta = \theta \times 100 = \left(\frac{(R_\mathrm{p})_\mathrm{inh} - R_\mathrm{p}}{(R_\mathrm{p})_\mathrm{inh}} \right) \times 100 \qquad (3)$$

where R_p and $(R_\mathrm{p})_\mathrm{inh}$ represent the values of polarization resistance in the absence and presence of inhibitor respectively. The values of polarization resistance, surface coverage and the inhibition efficiency for AA 2017A alloy in investigated caffeine solution were shown in Table 3. Polarization resistance and corrosion inhibition efficiency increase with increasing caffeine concentrations.

Table 3. Corrosion parameters for AA 2017A in 0.5 mol/dm³ NaCl solution in the presence of different concentration of caffeine, determined by linear polarization method

c_caffeine (mol/dm³)	R_p (kΩ cm²)	Θ	η (%)
0	3.83		
1×10^{-5}	8.70	0.5597	55.97
5×10^{-5}	9.99	0.6166	61.66
1×10^{-4}	10.89	0.6484	64.84
5×10^{-4}	12.94	0.7040	70.40
1×10^{-3}	14.85	0.7420	74.20

Using the linear polarization method, the influence of the stabilization time (up to 4 hours) on the inhibition of AA 2017A alloy corrosion with the highest concentration of caffeine (1×10^{-3} mol/dm³) was investigated and the results obtained were shown in Fig. 6. As can be seen, the polarization resistance increases with the stabilization time of alloy on E_OC, which means that the protective properties of the surface film are improved.

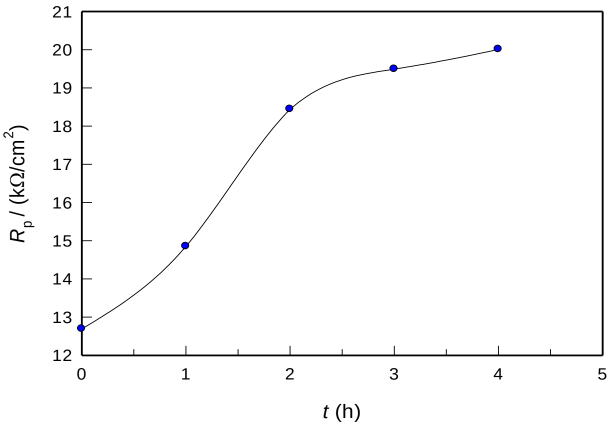

Fig 6. Change of polarization resistance of AA 2017A alloy with stabilization time in 0.5 mol/dm³ NaCl + 1×10^{-3} mol/dm³ caffeine solution

According to the obtained results the mechanism of caffeine action on AA 2017A alloy corrosion can be explained by the formation of the 3D surface layer consisting of inhibitor and products of corrosion. The formed surface layer acts as a physical barrier and prevents direct contact between metal and aggressive medium, and thus metal corrosion. Protective properties of the surface film are better if the inhibitor concentration is higher and the exposure time is longer.

Adsorption of caffeine

Adsorption of caffeine on the AA 2017A alloy surface was further characterised by fitting the experimental data to several adsorption isotherms. The Freundlich's isotherm isotherm (Eq. 4) was found to most suitably describe the adsorption behaviour of caffeine on AA 2017A alloy:

$$Kc^\mathrm{n} = \theta; \qquad 0 < n < 1 \qquad (4)$$

were K is the equilibrium adsorption constant. The relation between the equilibrium adsorption constant, K, and free energy of adsorption $\Delta G^\circ_\mathrm{ads}$, is given by:

$$K = \frac{1}{c_\mathrm{solvent}} \exp\left(\frac{-\Delta G^\circ_\mathrm{ads}}{RT} \right) \qquad (5)$$

where c_{solvent} represents the molar concentration of the solvent, which in the case of water is 55.5 mol/dm^3, R is the universal gas constant, and T is the absolute temperature. The Freundlich's isotherm can also be written in the form of:

$$\ln\theta = \ln K + n \ln c \qquad (6)$$

Accordingly, a linear relationship can be obtained when ln θ is plotted as a function of ln c, where a ordinate intercept represents ln K (Fig. 7).

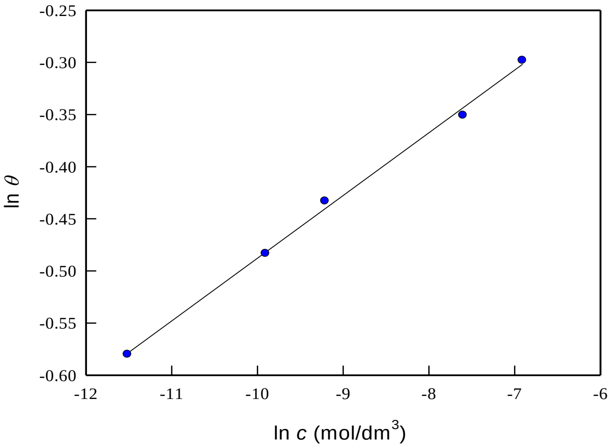

Fig. 7. The Freundlich adsorption isotherms of caffeine adsorption onto AA 2017A alloy surface in 0.5 mol/dm^3 NaCl solution determined by linear polarization measurements

The free energy of adsorption was calculated from experimental data and found to be equal to -9.93 kJ/mol. It is well known that values of $\Delta G^{\circ}_{\text{ads}}$ in the order of -20 kJ/mol or lower indicate a physisorption, while those of order of -40 kJ/mol or higher involve charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) (Donahue, Nobe, 1965). The adsorption free energy closes to -10 kJ/mol indicates physical adsorption of the caffeine on the AA 2017A alloy surface in NaCl solution.

Conclusions

The presence of caffeine causes significant changes in the polarization behaviour of the AA 2017A aluminium alloy. The reduction of the anodic and cathodic current density along with the slight changes the values of corrosion potential in the cathodic side can be observed. It can be said that the caffeine belongs to a mixed type of inhibitor, with higher influence on cathodic reaction.

Inhibition efficiency increased with caffeine concentration and the highest value of ≈ 76% was obtained with 10^{-3} mol/dm^3 caffeine.

The adsorption behaviour of investigated inhibitor can be described by the Freundlich adsorption isotherm. The adsorption free energy closes to -10 kJ/mol indicates physical adsorption of the caffeine on the AA 2017A aluminium alloy surface in NaCl solution.

The mechanism of caffeine action on AA 2017A alloy corrosion can be explained by the formation of the 3D surface layer consisting of inhibitor and products of corrosion. The formed surface layer acts as a physical barrier and prevents direct contact between metal and aggressive medium, and thus metal corrosion. Protective properties of the surface film are better if the inhibitor concentration is higher and the exposure time is longer.

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