

The Effect of the Action of Impurities Present in Methanol as a Basis for Automobile Fuel and Their Impact on the Environment

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Corrosion of the tank made of aluminum alloy AlMg2,7Mn (5454) has been studied by electrochemical methods in methanolic solution containing different concentrations of acid, chloride, sulphate and water as impurities. In all these cases, the alloy exhibited a sponge passivity. Adding a 1mM solution in fuel leads to a considerable increase in corrosion potential, a 1 mM chlorine solution decreases the pitting potential, and a 1 mM solution of sulfate concentrations does not show any change. In the first phase, due to the hydroxyl ion that surrounds the aluminum, the present water leads to a decrease in the pitting potential. At the same time, the combustion of fuel remains the biggest source of air pollution. The air is polluted by impurities (acids, chlorides, sulphates and water) present in fuels, smoke (incomplete combustion) or nitrogen and sulfur oxides, so it is required to keep them within the limits set by the rules in force.

Keywords: aluminium alloy, pitting potential, impurities, polarization curves, open circuit potential

Aluminum alloys are generally used for various applications such as construction, transport, machinery and various industrial equipment. Due to their mechanical properties, low density, good electrical and thermal conductivity, high ductility, corrosion resistance, these alloys are also used in the manufacture of automobile tanks [1-11].

However, it is well known that aluminum alloys are susceptible to corrosion, especially to pitting corrosion in aggressive solutions. This corrosion time is due to impurities present in car fuel [13, 26- 27]. The addition of corrosion inhibitors in the corrosive environment prevents corrosion, and this technique is known to be one of the most practical and effective means of preventing metal corrosion in acidic environments. Studies have shown that organic compounds containing multiple bonds in their molecules and heteroatoms such as N, O, S can be considered the most effective inhibitors for the corrosion of aluminum alloys in the acid and alkaline medium [12].

Studies regarding the inhibition of corrosion of aluminum alloys have shown that the most commonly used methods are: weight loss, hydrogen reduction and polarization [14,15].

As a result of the increasing use of alcohol (methanol, ethanol) as motor fuel, a special emphasis has been put on the characterization and understanding of the corrosion of metals and alloys in such solutions. Of particular importance in this case are the small impurities of acids, chlorides, sulphates and water present in alcoholic solutions.

Figure 1 shows an electrochemical cell on which different studies were conducted in methanolic solutions containing the above mentioned impurities, and an acceleration of the acidic corrosion process and an inhibition of the effect in aqueous medium was observed.

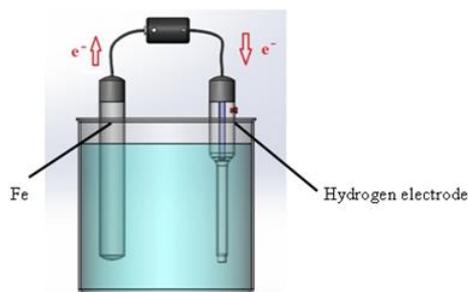
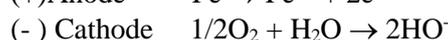
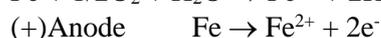
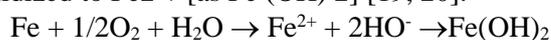


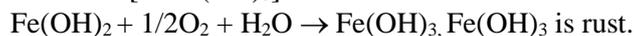
Fig. 1 Electrochemical cell containing a Fe electrode and a normal hydrogen electrode

Another example is the rusting of iron in water, with the dissolution of oxygen. This process takes place in two stages, in the first stage Fe is oxidized to Fe²⁺ + [as Fe (OH) 2] [19, 20].



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and in the second stage Fe^{2+} turns to Fe^{3+} [as $\text{Fe}(\text{OH})_3$].



So, as observed, any corrosion process in aqueous solutions involves oxidation of the metal and reduction of some species in the solution (electron acceptors), resulting in the transfer of electrons between the two reactants [21].

The metal-electrolyte interaction represents an electrochemical system [19, 20] of the galvanic cells category. There is a potential difference between metal and electrolyte as a result of the exchange of electrical charges between the two species, called electrode potential [20, 22, 23].

The previous studies have explained two primary empirical observations on the effect of acids on iron corrosion in methanolic solution, namely: the increase of the corrosion rate (15 times, given the addition of a 1mM acid solution) and corrosion potential (200mV given the addition of a 1mM acid solution) [24].

It has been shown that the effects of the acid are given by two separate phenomena: the acid passes the surface of the iron and the reduction of hydrogen is substantially faster than the reduction of oxygen in the acidified methanol solution. This last effect results in increased corrosion potential, which leads to increased corrosion speed.

The addition of watery solutions results in inhibition of iron corrosion in acidified methanolic solutions.

It was found that hydrogen reduction was substantially lower than mass transport control, relative to the corrosion potential of iron. The addition of water to acidic solutions reduces the corrosion rate by inhibiting H^+ mobility, thus reducing the H^+ diffusivity and thus the density of the diffusion limit current of the cathodic reaction in acidified methanolic solution [22, 23]. This reduction in the diffusion limit current directly leads to a decrease in corrosion speed. The reduction of hydrogen mobility is due to the solubilization of hydrogen, water in methanol. At low water concentrations, hydrogen concentration limits are important for conductivity.

Experimental part

Electrochemical studies were carried out on an aluminum alloy of the AlMg2,7Mn (5454) type according to DIN, in a methanolic solution containing different concentrations of acid, chloride, sulfate and water as impurities. In all these cases, the alloy exhibited a spontaneous passivity. Electrochemical experiments were carried out using a standard electrochemical three-electrode cell. A conventional three electrode cell was utilized in these experiments, with the aluminum alloy as the working electrode, a platinum wire and Ag/AgCl as the auxiliary and reference electrodes, respectively. The finely polished aluminium alloy specimens were exposed to corrosion medium in base solution and after addition of impurities 1mM acid, 1mM sulfates, 1mM chlorides, or 0.5% water, using an AUTOLAB Potentiostat (Model Reference-668). The Tafel plots were recorded by polarizing the specimen to -1.0 V cathodically and $+1.0$ V anodically with respect to the corrosion potential (E_{corr}). The aluminum alloy composition (in% of mass) of 2.46% Mg, 0.22% Fe, 0.19% Cr, 0.1% Si, 0.1%, 0.02% Ti and the rest Al is used as a material for the construction of automobile tanks and therefore the knowledge of the effects of impurities in methanol solutions is of particular importance.

In the basic solution, the aluminum alloy does not exhibit a manifestation of the passive transition as shown in Figure 2.

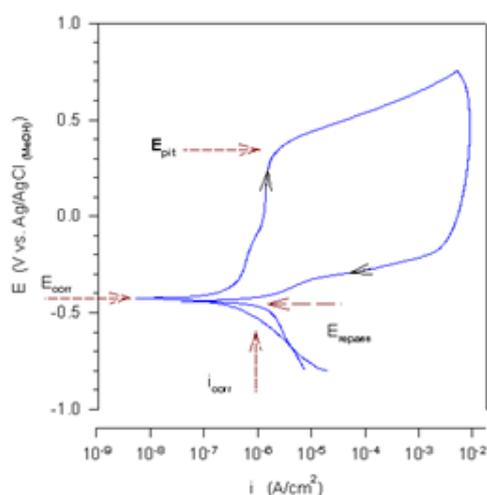


Fig. 2 Cyclic polarization curve for the aluminum alloy in the base solution (anhydrous methanol containing 0.1 M sodium perchlorate solution)

This lack of active-passive transition, in close correlation with the potential for corrosion, can be called spontaneous passivity. The passive region was limited to $+0.35$ V (SSC) by the corrosion points shown in Figure 3. Figure 4 shows the photomicrograph of the aluminum alloy surface after determining the polarization curve.



Fig. 3 Corrosion points on the surface of the tank

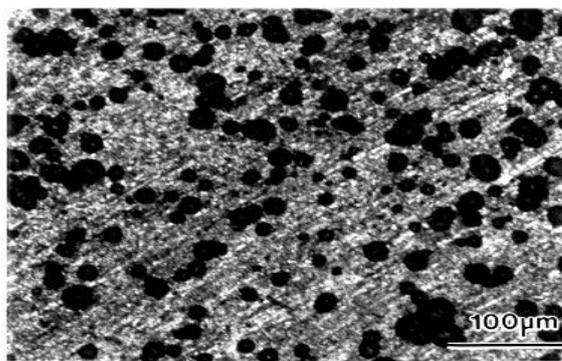


Fig. 4 Photomicrograph of the aluminum alloy surface after determination of the polarization curve

The effects of polarization due to the presence of impurities (1mM acid, 1 mM sulfates, 1 mM chlorides or 0.5% water) are shown in Figure 5.

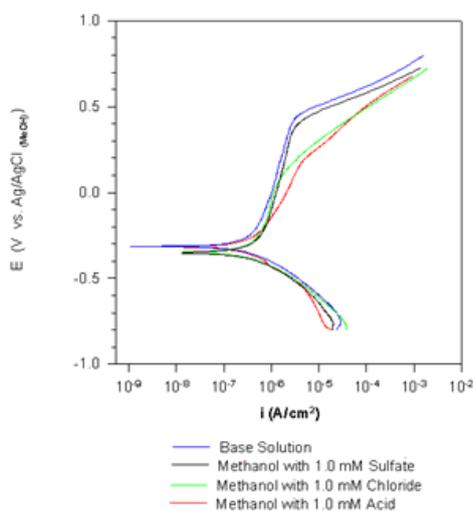


Fig. 5 Aluminum alloy polarization curves in base solution (a) and after addition of impurities (b) 1 mM acid, (c) 1 mM sulfates, (d) 1 mM chlorides, or 0.5% water

Figures 6 and 7 show the effects of impurities on the electrochemical parameters that characterize the corrosion processes when the water concentration increases or decreases. Corrosion speed did not have a total effect in any of the solution types, neither for a single solution nor in combination. The solution containing acids was the only one that influenced the corrosion potential.

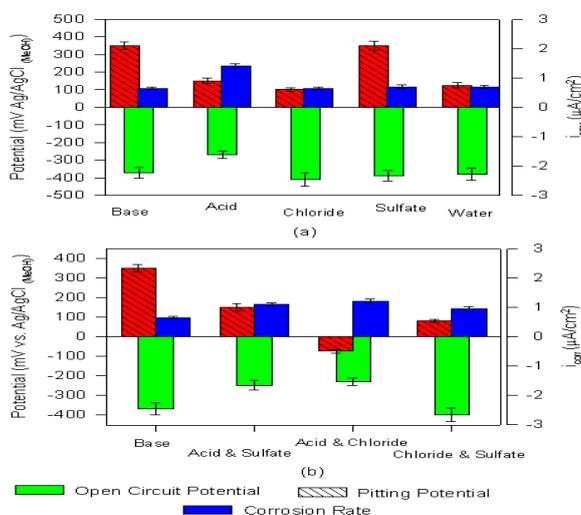


Fig. 6 Effects of single impurities (a) and their combinations (b) on the corrosion potential and corrosion speed of the aluminum alloy. All solutions contain sodium perchlorate and <0.06% water (mass percent)

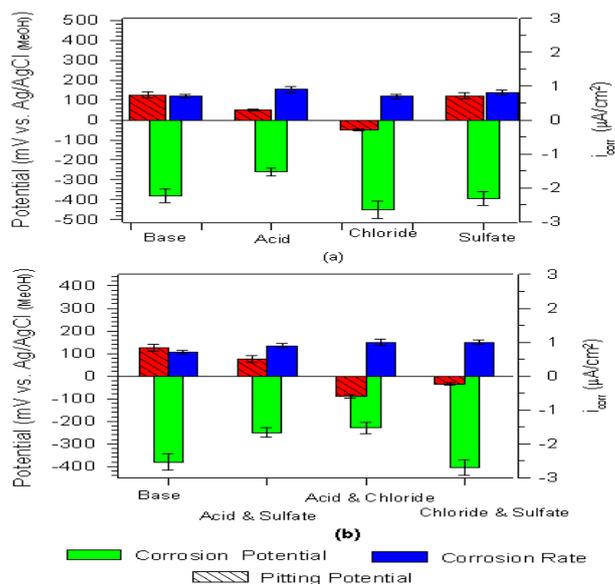


Fig. 7 Effects of single impurities (a) and their combinations (b) on the corrosion potential and corrosion rate of the aluminum alloy. All solutions contain sodium perchlorate and 0.5% water (mass percent)

The solution containing water and acid leads to a decrease in the pitting potential as seen in figure 8.

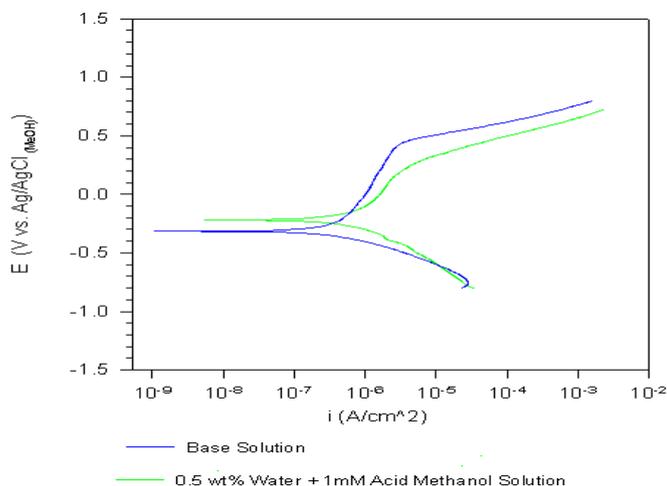


Fig. 8 Polarization of the aluminum alloy in the base solution (a) and addition of 1 mM acidic solution and 0.5% water (mass percent). The passivity interval decreases when two impurities are added

It is noted that in the case of aluminum alloy activated by 1mM acid, the quantitative water effects are much weaker than those for Fe, which have active corrosion in 1mM acid [20].

The combustion of fuel produces a large amount of chemicals that are emitted into the atmosphere. In fact, fuel consumption contributes significantly to air pollution. Studies carried out between 2015-2018 on emissions in the transport sector accounted for approximately 37% of the total emissions inventory on the territory of our country. The pollutants resulting from burning fuel as the particles, nitrogen oxides, volatile organic compounds, benzene, sulfur dioxide and metals. Many of these pollutants contribute to smog formation.

Engine emissions vary greatly depending on the type, age and condition of the engine, how it is used and the type of fuel. Exhaust fumes are a complex mixture of hundreds of chemicals, in gaseous or particulate form. Nitrogen oxides, carbon monoxide, formaldehyde, acetaldehyde, benzene, polycyclic aromatic hydrocarbons and aromatic polycyclic aromatic hydrocarbons are among the emissions from combustion. Exhaust gas particles give a carbon core that absorbs organic compounds, nitrates, sulfates, metals and other trace elements.

It is known that transport is the main source of atmospheric air pollution, emitting large amounts of hydrocarbons, carbon oxides, nitrogen oxides etc. in the air. Their share in the total volume of releases at the country level is about 90%, and at the level of Dâmbovița County more than 95%. The dynamics of air pollutant emissions from mobile sources between 2015 and 2018 and their component distribution are shown in Figure 9 (a, b, c, d).

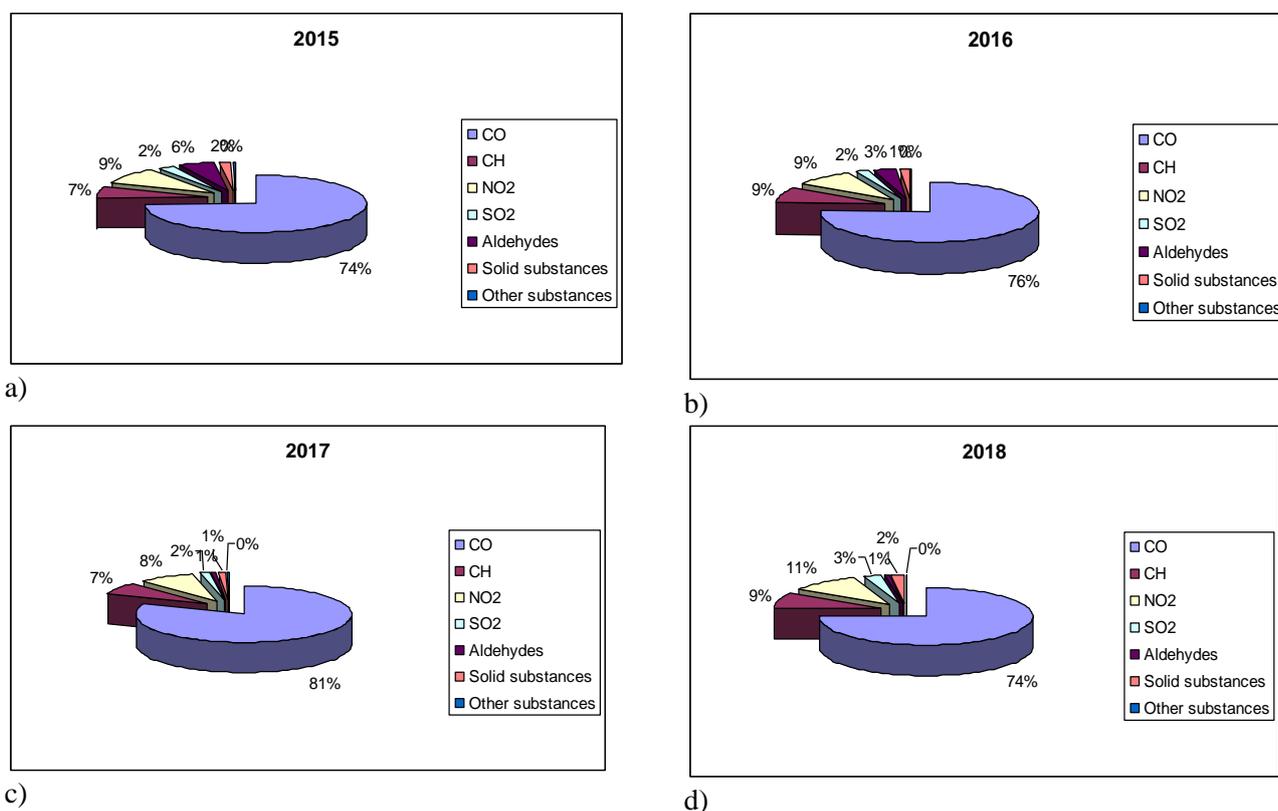


Fig. 9 The dynamics of pollutant emissions from atmospheric pollutants from mobile sources during the period 2015-2018 [25]

The most polluting source is car transport, which accounts for about 93% of total emissions. The largest share of the pollutants of mobile sources - car transport (Figures 9a, b, c, d) is carbon dioxide (about 76.85%, hydrocarbons (about 12.55%) and nitrogen dioxide, 05%).

Results and discussions

In all the solutions studied, the aluminum alloy exhibits a spontaneous passivity (as shown in Figure 2) as evidence of forming a stable film on the surface of the alloy upon contact with the methanol solution or opening the potential of the circuit.

It has also been observed that the effect of sulphates, chlorides, acid and water is similar to that observed for Fe, while the corrosion parameters (corrosion rate, corrosion potential) are much lower.

A particular case is the low acidity of the methanol solution. Thus, the tanks made of the aluminum alloy of the studied composition behave better at corrosion than a steel. It should be specified that 1mM acid substantially increases the corrosion potential of the aluminum alloy (ca. 200mV), while the pitting potential decreases by 100mV (Figure 5). This decrease in passivity increases the likelihood of a stable pitting in open circuit conditions. As observed in the case of iron, sulphate has no effect on the corrosion of the aluminum alloy (Figures 6 and 7).

In Figure 5 it was observed that the addition of 1 mM acid solution increased the corrosion potential of the aluminum alloy with 100mV. This increase results from the introduction of an additional cathodic reaction (proton reduction) with faster kinetics than the reduction of oxygen (which is the predominant cathodic reaction in neutral methanol). Unlike iron, the low acid addition does not attack the surface of the aluminum alloy, the corrosion rate is slightly increased due to the low increase in the current density with the potential (Figure 2) in the passivity zone.

The addition of 1 mM of the acid can reduce the pitting potential of the 200 mV aluminum alloy, which combined with a 100 mV increase in the corrosion potential, significantly decreases the passivity among the alloys (Figure 8). The addition of water influences very little the corrosion rate on the aluminum alloy, even in the presence of acid. This has not been done because the surface of the alloy remains passive. Under these conditions, decreasing the proton reduction current due to the addition of water will not have an effect on the corrosion rate, the corrosion potential of the aluminum alloy being in the active region of the proton reduction reaction in methanol.

Conclusions

By adding a 1mM acid solution, a considerable increase in the corrosion potential is observed; a 1mM chloride solution decreases the pitting potential, and a 1mM solution of sulfates does not make any changes. In the first phase, water seems to decrease the pitting potential due to the aluminum surrounded by hydroxyl ions. The secondary interactions that appear are of no significant significance.

By the ability of water to form a passive film in non-aqueous solutions, particularly under acidic conditions, there is a change in the pitting potential.

An explanation of the obtained results shows the small influence of water on the pitting potential, as a result of the increase in the stabilization of the pitting by the production of metastable pitches resulting from the hydrolysis of the aluminum ions.

The noxious effects of acid have been shown to be given by the cathodic oxidation reaction (proton reaction), which is less kinetic than oxygen reduction despite the increased oxygen concentration.

Adding water to acidify methanol inhibits the increase of corrosion rate by activating material corrosion, which reduces the protonation velocity corresponding to the preferential solubilization of protons in water.

The effects of 1mM chlorides, sulphates and acid on the aluminum alloy are similar to those of iron; all effects have a lower magnitude in the aluminum alloy, indicating that the aluminum alloy is more resistant to the action of the impurities present in methanol as the fuel base.

The noxious effect of water on pitting potential was explained on the basis of competition between the effects of stabilizing the pitches of hydrolysed Al^{3+} ions and blocking the diffusion limit current by reducing the protons. Thus, water which is generally a good inhibitor of corrosion in acidified organic solvents, the addition of small amounts of water in acid-containing methanol solutions as impurity causes an increase in the probability of occurrence of the pitting for the aluminum alloy.

When increasing the water content, the stabilization of the pitting is restricted by the inhibition of the cathodic reaction occurring on the passive surface. This effect of the cathodic reaction overcomes the effects of hydrolysis water and the action of water as an inhibitor of increased concentrations.

The main sources of atmospheric air pollution in Dâmbovița county are the production of electric power at thermal power stations, heating systems for dwellings, auto traffic, air and industrial activity.

Car transport is the main source of fuel consumption and the release of toxic substances into the atmosphere. The highest share of pollutants is C-oxide, hydrocarbons and nitrogen dioxide.

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Manuscript received: 29.05.2019

