INFLUENCE OF A COOLING LIQUID
ON THE CORROSION BEHAVIOUR OF AlMn ALLOY

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Electrochemical behaviour of AlMn alloys was determined by stationary electrochemical methods: potential versus time, polarization curves and linear polarization resistance recorded at different temperatures in a commercial cooling liquid, Glaceol D, which contains tolyltriazole as a corrosion inhibitor. The later was found to be an anodic corrosion inhibitor. The inhibition efficiency increases as the added concentration of the cooling liquid is increased (95% for 50%vol. Glaceol D). At the ambient temperature, the corrosion resistance of this aluminium alloy is increased with the immersion time, unfortunately at higher temperatures the corrosion rate is increased too. The intermetallic particles, such as $Al_6(MnFe)$ and α-Al(Mn,Fe)Si, were found to be the cathodic sites for the corrosion of aluminium matrix.

INTRODUCTION

3xxx alloys, as a series of aluminium alloys containing Mn as main alloying element, are widely used in a variety of industry fields; including the automotive industry.[1] The AlMn alloys have been broadly integrated into vehicular exchange systems, replacing the stainless steel or copper.[2] In commercial alloys, iron and silicon are invariably present as impurities and sometimes copper, magnesium and zinc are also added as minor alloying elements. During solidification, constituent particles are forming in the alloy mainly as interdendritic eutectic networks.[3, 4] The $AlMn_6$, $Al_6(MnFe)$, α-Al(Mn,Fe)Si or $FeAl_3$ (formed if there is more Fe than Mn in the particles) are the main intermetallic inclusions in AlMn alloy. However, the intermetallic particles, which confer superior strength to the alloy, also can form galvanic couples in moisture promoting localized corrosion processes. For instance the corrosion potentials of aluminium and $AlMn_6$ are

similar, while the one of $Al_6(MnFe)$, α-Al(Mn,Fe)Si or $FeAl_3$ is more cathodic. The beneficial effect of manganese in commercial Al-Mn alloys has been rationalized on the basis that is combined with iron to form the phase $Al_6(Mn,Fe)$ which will decrease the potential difference between the matrix and the intermetallics and consequently to reduce the extent of overall corrosion.[5] In order to avoid this drawback and to offer a better protection for these alloys new environmental-friendly corrosion inhibitors have been actively developed in the recent decades. The triazole and tolytriazole were investigated in many works as corrosion inhibitors for aluminium alloys, copper and its alloys in chloride solutions.[6-9] Recently these compounds were also studied from the point of view of their inhibition effect for aluminium alloys and show promising results.[9] It has been suggested that anodic oxide films might control the corrosion resistance of the base metal. However, the mechanism of corrosion protection is still not clear.

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The aim of this study is to evaluate if this commercial cooling liquid, Glaceol D, has a good formulation to prevent the aluminium alloy, 3003 corrosion.
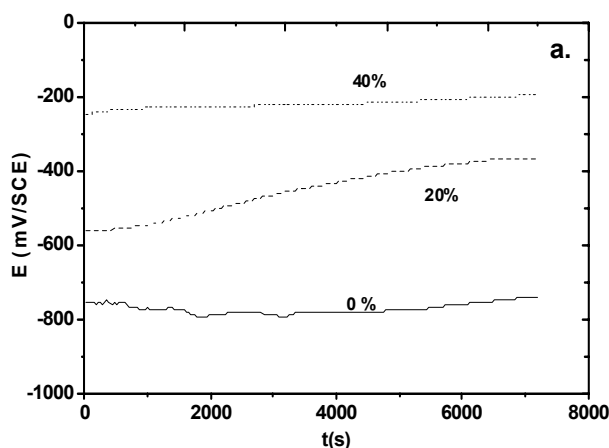
EXPERIMENTAL

The specimens of aluminium alloy 3003 are elaborated by Vitmetco Alro, Roumania. The AlMn alloy presents the followed chemical composition (wt %): Si 0.2, Fe 0.4, Cu 0.15, Mn 1.05, Mg 0.003, other elements 0.4 and the rest is Al. After cutting in small pieces (about $1.5*2$ cm^2), an electrical connection is assured by a welding cooper wire, then they are coated with a masking paint to determining the active area.

They are etched in NaOH (40 g/L) for 5 min to destroy the natural aluminium oxide layer. Finally they are degreased in alcohol ultrasonic bath for 2 min and dried with hot air.

The so prepared samples constitute the working electrode of the experimental device. This later is composed too of a reference electrode (SCE, saturated calomel electrode) and of a carbon counter electrode.

The coolants used in automotive cooling loops are mainly composed on ethylene glycol and water (pH between 7 and 8). The electrolytic solution is based on a commercial cooling liquid, Glaceol RX D, which is diluted with deionised water and it is added 100ppm NaCl. The commercial cooling liquid contains 92% ethylene glycol, tolyltriazole 0.2 vol.% as corrosion inhibitor and salts. A blank solution (without any inhibitor) was used in order to simulate the general composition of a cooling liquid, it contains ethylene glycol 30%vol., deionised water and 100ppm NaCl. The solution volume is of 150 cm^3.

In an automotive system, the working temperature range depends on the geographic locations, although the maximum coolant temperature is always about 100°C, the minimum can fall down at about -30°C, so different working temperatures (25, 40 60 and 80°C) were used in the present study.

An EGG PAR potentiostat (model 263 and 273) allows performing the experiments. It is connected to a computer device (software M352) in order to pilot the tests and record the results. Different types of measures are performed: free corrosion potential versus time, potentiodynamic curves and polarization resistance evolution versus time and temperature.

The inhibition efficiency IE was calculated using the following equation:

$$I(E\%) \quad \frac{i \quad i_{inh}}{i} \quad 100 \qquad (1)$$

Where: i and i$_{inh}$ are the corrosion current densities in free and inhibited solutions, respectively.

An optical microscope Olympus was used to study the surface evolution of the 3003 alloy after the immersion tests.

RESULTS AND DISCUSSION

Electrochemical study at the room temperature

Fig. 1a presents the evolution of the free corrosion potential of AlMn alloy in time (2h of immersion) at the room temperature in the electrolyte solution (with ethylene glycol or with Glaceol D+100ppm NaCl). It is seen that in the absence of Glaceol D, the free potential of AlMn alloy presents small variations in the first period of immersion; on the other side for the same period in the Glaceol D medium (20%vol.) it can be observed an increase of the potential, which means that on the metallic surface is formed a protective inhibitor film. It can be noted also that for the all solutions the free potential reaches a constant value at the end of the immersion period.
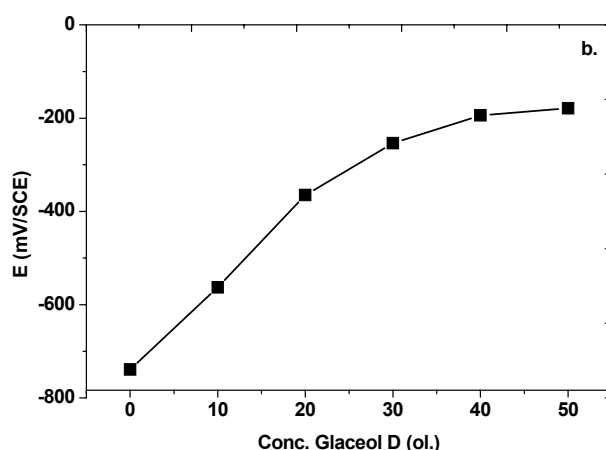

Fig. 1 – Free potential evolution of AlMn alloy as a function of time (a) and as a function of Glaceol D concentration in vol.% (b) at the room temperature.

Fig. 1b presents the free potential evolution of AlMn alloy as a function of Glaceol D concentration at the room temperature, after 2h of immersion. When the concentration of the Glaceol D increases it can be observed a continued increase of the free potential (from -742 to -192mV/SCE);

on the other hand when in the tested solution is added more 40%vol. of Glaceol D it can be observed that the free potential does not change, it remains constant (-200mV/SCE).

To estimate the effect of the inhibitor on the anodic and cathodic partial electrode reactions, potentiodynamic polarization measurements were carried out in the potential range from -250 mV to 900 mV versus open circuit potential (OCP) with 0.166 mV/s potential sweep rate. Fig. 2a shows the polarization curves of AlMn alloy in the electrolyte solution with and without Glaceol D after 2h of immersion.

The cathodic log i vs E curve in the inhibitor-free ethylene glycol solution shows a diffusion-limited plateau of the cathodic current at E < -825mV/SCE (thus - 43mV/OCP). Introduction of the Glaceol D into solution doesn't lead to a decrease of the cathodic current (Fig. 2a). The cathodic process is represented by the oxygen diffusion process. It is seen that the addition of Glaceol D in different concentrations displaces the corrosion potential to the more anodic values and leads to a decrease of the anodic corrosion current densities. It can be also observed that the curves change their forms; it appears a large anodic domain of passivation.

In order to see the effect of the intermetallic particles, tests on pure aluminium electrode were carried on. The comparison between AlMn and Al (Fig. 2b) shows that the alloy is a little more sensible to corrosion than aluminium. This difference is caused by the intermetallic particles present in the surface of AlMn, the latter being nobler and so responsible of a galvanic coupling prejudicial to Al.

The electrochemical parameters, E_{corr}, i_{corr} and the Tafel coefficients (β_a and β_c) have been determined from the polarization curves. These parameters give information about the inhibitor nature, its efficiency and the modifications on the reactions mechanism with the temperature respectively. It was found that the i_{corr} decresead with the increase of the Glaceol D concentration ($1.91\mu A/cm^2$ to $0.09\mu A/cm^2$ for 0 to 50%vol. Glaceol D) and that E_{corr} is moved in the positive direction (from -742 to -179mV/SCE for 0 to 50%vol. Glaceol D). The values of anodic Tafel constants are changed in the presence of Glaceol D. All these results reflect the effect of the tolytriazole on the anodic reaction. Therefore, it can be concluded that tolytriazole acts as an anodic inhibitor.

From the electrochemical parameters it can be possible to determine a parameter (θ), which represents the part of the metal surface covered by the inhibitor molecules. The followed equation was used to determined θ:

$$\theta = \frac{i - i_{inh}}{i} \qquad (2)$$

The later one was calculated for different Glaceol D concentrations and it seems that θ increases as the Glaceol D concentration (C) is increased. Plotting C/θ against C (Fig. 3) gives a straight line up to 10%vol., indicating that the adsorption of tolytriazole on surface of aluminium manganese alloy follows Langmuir isotherm. That is not verified at small concentrations. From this result it can be concluded that there is no interaction between the molecules adsorbed at the metal surface.
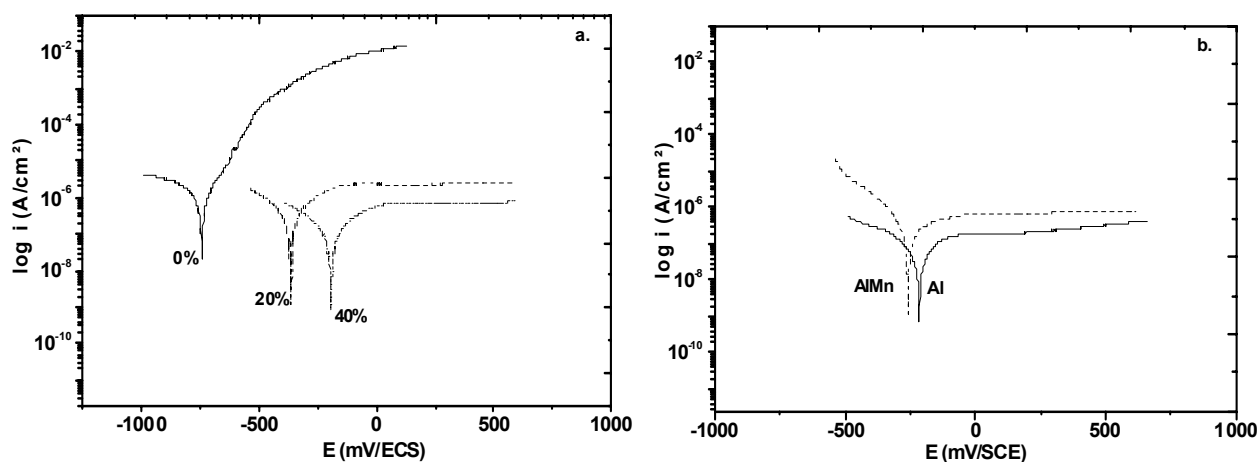

Fig. 2 – Polarization curves at the room temperature after 2h of immersion: (a) for AlMn alloy in Glaceol D in different concentrations (0 to 50%vol.) + 100ppm NaCl and (b) for Al and AlMn alloy in Glaceol D 30% +100ppm NaCl.
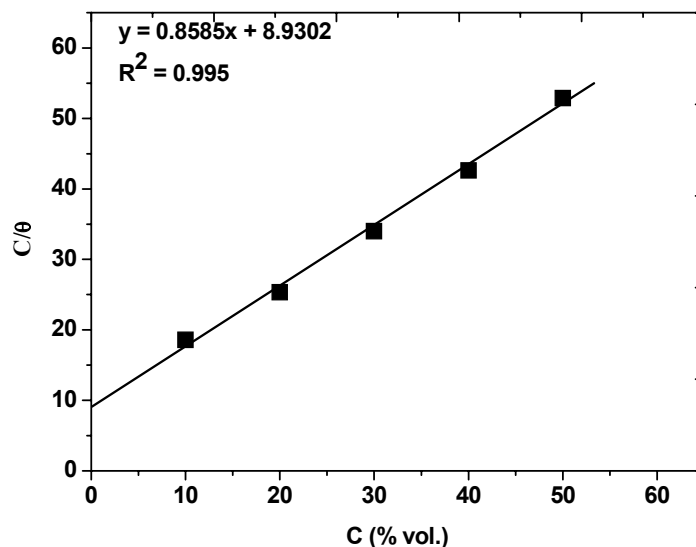
Fig. 3 – Adsorption isotherm of tolytriazole on AlMn alloy surface in Glaceol D medium at the room temperature.

Influence of the temperature

Mostly the increase of the temperature is favorable for the various reactions processes at the metal-solution interface. Fig. 4 presents the evolution of the linear polarization resistance as a function of immersion time and temperature.

It can be noted that the corrosion resistance of AlMn electrode increased with the immersion time (even over 80°C), period in which the inhibitor film formation takes place. But, unfortunately, it can be seen too, the corrosion resistance of the film formed decreases with the increase of temperature. So, if the temperature of electrolyte solution rises, then the concentration of the dissolved oxygen is decreased, this enhances the aluminium dissolution. It is well known that intermetallic particles containing Mn, Fe and Si are present at the surface of AlMn alloys, it seems that the aluminium oxidation takes place all around these particles, preferentially near the rich Fe particles.[10] Fig. 5 presents the optical microscopically images for AlMn alloys after immersion in Glaceol D solution at different temperatures (25, 40, 60 and 80°C). It can be observed that starting at 40°C the metallic surface is increasingly covered by the oxide film. It has been supposed that this film formed contain a combination of oxides (including Al, Mn or Fe oxides) and tolytriazole inhibitor.
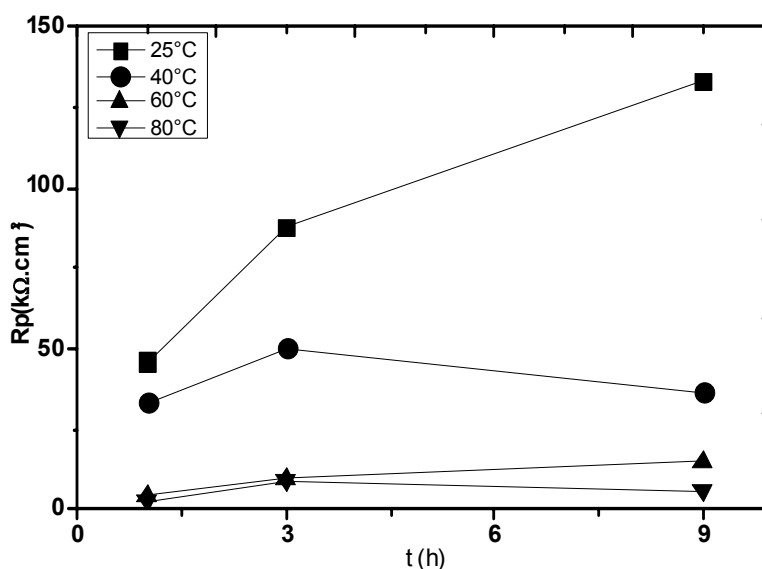

Fig. 4 – Linear polarization resistance evolution as a function of immersed time
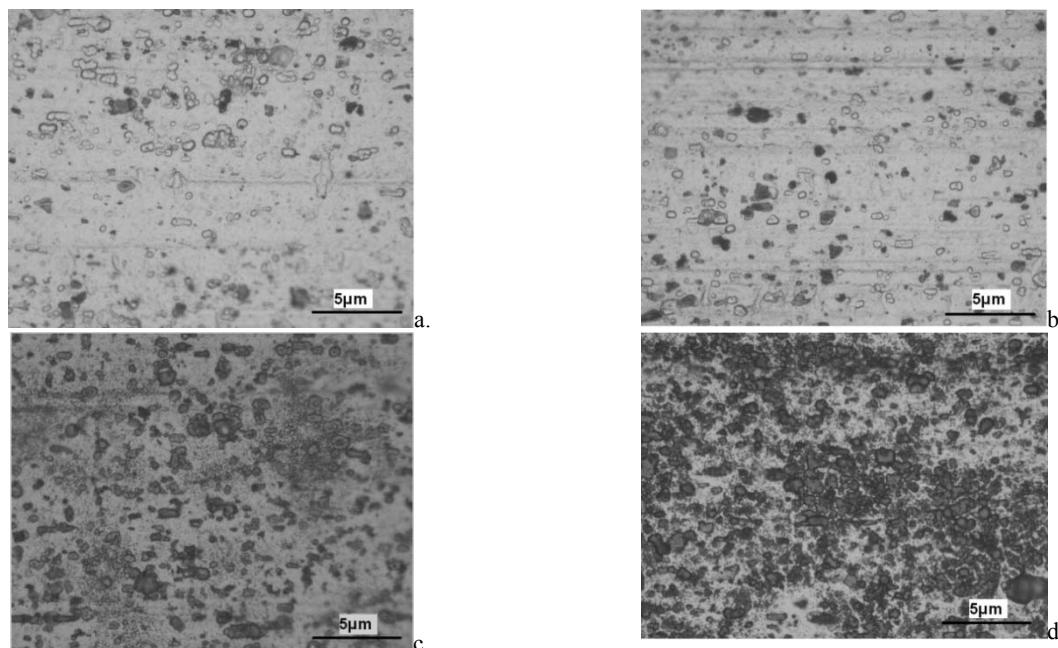and temperature for AlMn alloy in Glaceol D 30%vol. +100ppm NaCl.

Fig. 5 – Optical microscopic images for AlMn alloy after immersion in Glaceol D solution at different temperatures (a. 25°C, b. 40°C, c. 60°C and d. 80°C).

To observe the efficiency of the tolytriazole inhibitor and the electrochemical behaviour of AlMn alloy thermal cycle's tests were performed (the results are presented elsewhere[10]). It was observed that even if at 80°C the inhibitor efficiency decreases, after one thermal cycle, when the solution temperature is about 25°C, the inhibitor film is reformed on the metallic surface. So, it can be concluded that tolytriazole inhibitor is stable with temperature but it is possible that its adsorption may be a little bit less stable at high temperature. Because of that the film could be broken and the aluminum dissolution occurs.

CONCLUSION

Electrochemical tests were carried out in order to determine the electrochemical behaviour of AlMn alloy in a commercial cooling liquid, Glaceol D. This cooling liquid contains tolytriazole as corrosion inhibitor which was found to influence the anodic partial reactions. The inhibition efficiency increases as the added concentration of the cooling liquid is increased. The tolytriazole adsorption on the AlMn surface follows Langmuir isotherm. The corrosion resistance of aluminium alloy increases with the immersion duration. At higher temperatures (till 80°C), the dissolution of aluminium was found to be localized around the intermetallic particles rich in Fe, such as $Al_6(MnFe)$ and α-Al(Mn,Fe)Si,

which sustains the fact that those particles are the cathodic sites for aluminium matrix. The thermal cycles confirm that tolytriazole inhibitor is stable with temperature but it is possible that its adsorption may be a little less stable at higher temperatures.

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