The Inhibition of Corrosion for Metal Matrix Composites Reinforced with Nano Alumina in Al–Fao Water by Thiourea

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ABSTRACT:

In the present investigation, the static electrochemical corrosion behavior of nano $(Al_2O_3)_P$ based aluminum in Al –Fao water with and without inhibitor was compared. The nanocomposites were fabricated by using liquid metallurgy technique. The effect of inhibitors for nanoparticulates weight percentage on the corrosion rate was studied. The corrosion rate was increased by increasing weight percentage of the nanoparticles, the Al/ 5% nano $(Al_2O_3)_P$ composites exhibited the highest corrosion resistance among all the investigated nanocomposites with and without inhibitors. The obtained results signified that the mechanism of adsorption of thiourea molecules on the MMC surface was by physisorption.

Keywords: Corrosion inhibition, Thiourea, Nano alumina (Al_2O_3), Stir casting, Corrosion rate, Potentiostatic measurements, Al – Fao water.

تثبيط تآكل المواد المتراكبة المعدنية المقواة بدقائق نانوية للألومينا في ماء الفاو بأستخدام مثبط الثايوريا

الخلاصة:

تم في هذا البحث الحالي تقييم السلوك التاكلي بالمجهاد الساكن للالمنيوم المدعم بدقائق نانوية من الالومينا في ماء الفاو بوجود وغياب المثبطات. تم تحضير المواد المتراكبة النانوية بتقنية ميتالورجيا الحالة السائلة و دراسة تأثير المثبطات للدقائق النانوية المدعمة بنسب وزنية مختلفة على معدل التاكل.
وقد تبين ان معدل التاكل يزداد مع زيادة النسب الوزنية للدقائق النانوية حيث تبين بان المادة المتراكبة المدعمة بنسبة 5% من دقائق الالومينا النانوية هي الاكثر مقاومة تاكل من بقية المواد المتراكبة النانوية بوجود وغياب المثبطات.
اظهرت النتائج بان الثايوريا أسهمت في تكوين طبقة حماية على سطح المادة المتراكبة بواسطة ظاهرة الامتزاز الفيزياوي.

INTRODUCTION

Metal matrix composites (MMCs) are engineered materials formed by the combination of two or more materials, at least one of which is a metal, to obtain enhance properties. MMCs tend to have higher strength/density and stiffness density ratio, compared to monolithic metals. They are also tending to perform better at higher temperatures, compared to polymer matrix composites. Aluminum and magnesium are lightweight materials, when compared to iron and steel [1].

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Metal matrix composite (MMC) is normally fabricated by using a ductile metal (e.g., Al, Ti or Ni) as a base material, which is reinforced with ceramic (e.g., alumina, SiC, or graphite). Combining the metallic properties such as good ductility and toughness of matrix with ceramic properties such as high strength, hardness and elastic modulus of the reinforcement, the composites exhibiting good wear resistance can be obtained. Consequently, they have extensities interest from defence, aerospace and automotive industries and become very promising materials for structural applications as well. Particulate reinforced MMCs are promising because of their homogenous and isotropic material properties, low cost and ability to be formed using conventional metal processing techniques. Among the many ceramic reinforcements SiC has been found to be excellent capability with the Al-matrix [2-4].

Aluminum matrix composites (AMCs) exhibited better resistance to mechanical wear than their alloy. One of the main disadvantages of metal matrix composites is the influence of reinforcement on corrosion rate. This is particularly important in aluminum alloy based composites, where a protective oxide film imparts corrosion resistance. The addition of a reinforcing phase could lead to discontinuities in the film, thereby increasing the number of sites where corrosion can be initiated and making the composites more susceptible for corrosion in salt medium [5].

Recently, metal matrix nanocomposites (MMNCs) have become more attractive in various applications because of their improved mechanical properties over conventional micro-particle reinforced MMCs. These materials are expected to exhibit good corrosion resistance in the aggressive environments. Therefore, determination of the corrosion resistance of composite materials reinforced with nanoceramic additives is very important. Most studies conducted on Al matrix nanocomposites, have been focused on the corrosion susceptibility in NaCl solutions [6,7].

Experimental procedure:

Materials

Metal matrix composites containing various weight percentages of nano Al_2O_3 particles were produced by liquid metallurgy route. For the production of MMCs, a pure aluminum was used as the matrix material while Al_2O_3 particles with an average size of 30 nm were used as the reinforcement. The chemical composition of commercial purity aluminum (AA 1060) is shown in table 1 and the characterization of nano Al_2O_3 and reinforcing materials are shown in table 2.

Table (1) The composition of Commercial Purity aluminium (AA 1060)

Al %	Si %	Fe%	Ti%	V%	Cu%	Mn%
99.76	0.08	0.15	0.001	0.007	0.001	0.003

Table (2) The characterization of α- Alumina ceramic nanopowders

Alumina properties	
Purity	99+%
Particle size	30 nm
color	White Powder
Density	3.69 g/cm^3
Morphology	nearly spherical
Crystal Phase	A_2O_3 nanopowder **(α)**

Composite preparation

A stir casting setup (Figure. 1), which consisted of a resistance furnace and a stirrer assembly, was used to synthesize the composite. The stirrer assembly consisted of a graphite blades stirrer, which was connected to a variable speed vertical drilling machine (speed 0 to 1000 rpm) by means of a steel shaft.

The stirrer was made by cutting and shaping a graphite block to desired shape and size manually. The stirrer consisted of three blades at angles of 120° apart. Graphite crucible of 100g capacity was placed inside the furnace. Preheating of Alumina and Silicon Carbide mixture at 750°C was done for one hour to remove moisture and gases from the surface of the particulates [8]. The stirrer speed was then lowered vertically up to 3 cm from the bottom of the crucible. The speed of the stirrer was gradually raised to 800 rpm the preheated Alumina and Silicon Carbide particle was added with a spoon at the rate of 10- 20g/min into the melt.

The speed controller maintained with constant speed, as the stirrer speed got reduced by 50-60 rpm due to the increase in viscosity of the melt when particulates were added into the melt. After the addition of Alumina and Silicon Carbide particle, stirring was continued for 10 min. get better distribution. The melt was kept in the crucible for one minute in static condition, The slag were removed and Aluminium melt poured in the graphite moulds.

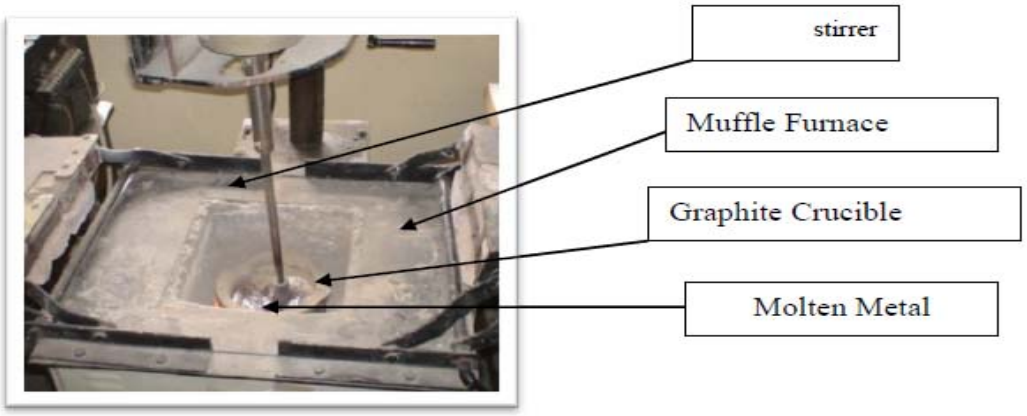


Figure (1) Stir casting set up.

Specimen Preparation for corrosion measurement

Mounting

The mounting process was performed by using XQ-2B mounting press, where the specimen was placed with phenolic resin in mold and heated up to 140^{o}C under pressure of 3500 – 4000 psi, for 5 – 10 min. For electrochemical studies, suitable provision was made on the other side for electrical contact.

Grinding and Polishing

The mounted specimens were ground with SiC emery papers to get flated scratch free surface in sequence of 400, 600, 800, 1000, and 2000.

The specimens were polished using polish cloth and alpha alumina 0.5μm and 1μm, and then washed with distilled water. The polished specimens then immersed with acetone, dried and used for microstructure evolution and electrochemical investigation.

Polarization Test

All experiments were carried out by using a three electrode, cell with saturated calomel electrode (SCE) as reference, platinum electrode as counter electrode and the cylindrical specimens of the alloy with active flat disc of (0.78 cm^2) as the working electrode. The SCE was connected via Luggin capillary, the tip of which was held very close to the surface of the working electrode to minimize the IR drop. Open circuit potential (OPC) measurements were recorded for 15 minutes, the time necessary to reach quasi stationary state for open circuit potential, Followed by polarization measurements at a scan rate of 3 mV/s for Tafel plots.

Fig. (2) shows the experimental arrangements for electrochemical measurement. All tests were carried out at room temperature. Table (3) shows the compositions of Al - Fao water.

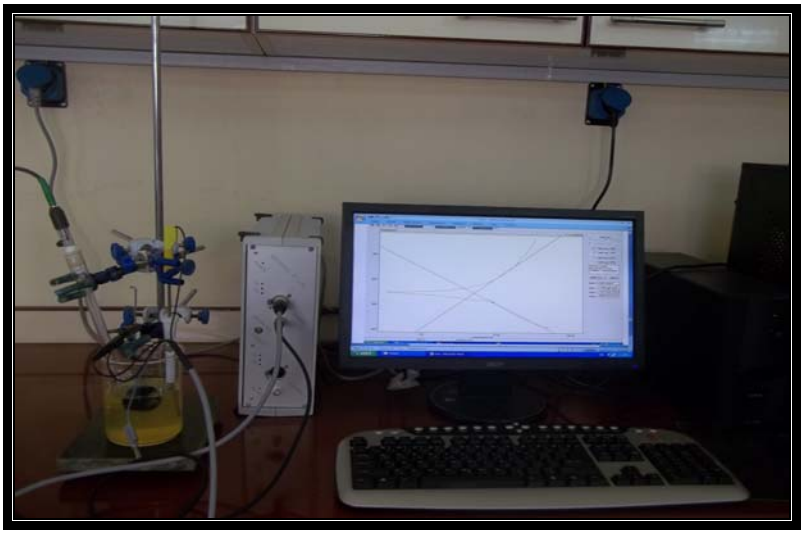


Figure (2): Experimental arrangements for electrochemical measurement.

In order to find corrosion rate from the following equation [9]:

$$\text{Corrosion rate (mm/y)} = \frac{3.27 \times 10\text{-}3 \times i\text{corr} \times \text{EW}}{\text{D}} \quad \text{....(1)}$$

Where ,

i_{corr} in (□A/cm^2) is the corrosion current density□ EW is the equivalent weight of the corroding species, and D in (g/ cm^3) is the density of the corroding species.

Table 3 shows the characterization of Al - Fao water.

Anions g/L	**Cl^-**	**7.04**
	SO_4^{2-}	**1.27**
pH		**7.6**
Electrical conductivity		**19.92 mS/cm**

The values of corrosion current (i_{corr}) were obtained from the point of intersection of both linear parts of the anodic and cathodic polarization curves with the stationary corrosion potential (E_{corr}). The inhibition efficiency (I.E.) obtained from the polarization curves is calculated using the following equation [10]:

$$\% \text{ I.E} = \left(1 - \frac{i_{add}}{i_{free}}\right) \times 100 \quad \ldots (2)$$

where
i_{add} and i_{free} are the current measured in the presence and absence of the inhibitor, respectively**.**

Selected Inhibitor

To study corrosion inhibition, thiourea was used with (0.01 w/v%) concentration which were prepared by weighting certain amount of thiourea in Al - Fao water. The experiments were carried out at room temperatures.

Thiourea is an organosulfur compound with the formula $SC(NH_2)_2$. Figure (3) illustrated the chemical structure of a thiourea. Table (4) shows physical properties of thiourea.

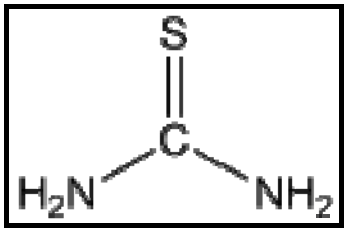


Figure (3) The chemical structure of a thiourea.

Table (4) Physical Properties of Thiourea.

Properties	
Molecular formula	CH_4N_2S
Molar mass	76.12 g/mol
Appearance	white solid
Density	1.405 g/ml
Melting point	182 °C; 360 °F; 455 K
Solubility in water	14.2 g/100ml (25°C)

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a common technique for organic compound characterization. FTIR was used to determine the composition and chemical structure of the inhibitors. The film formed on the MMCs surface (after immersion in Arab gulf water at 25^{o}C for 15 days) is carefully removed and analyzed. The FTIR- Fourier Transform Infrared Spectroscopy shown in Fig. (4).

Figure (4) Fourier Transform Infrared Spectrophotometer (FTIR)

Results and Discussion

Corrosion Behavior in Al – Fao water with and without thiourea

The corrosion parameters of composites in Al – Fao water are given in Table (4). The corrosion current density i_{corr}, increases with increase of Al_2O_3 content in the composites, corroborating the results that reinforcement with ceramic does influence and increase the corrosion rate of the aluminum matrix.

Table (4) Corrosion parameters of Al/nano $(Al_2O_3)_p$ composites in Al –Fao water with and without inhibitors.

Composites	Weight %	AL –Fao Waterwithout thiourea			AL –Fao Waterwith thiourea			IE%
		i_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion Rate (mm/y)	i_{corr} (A/cm^2)	E_{corr} (mV)	Corrosion Rate (mm/y)	
Al/ nano$(Al_2O_3)_p$	5%	4.12	-661.3	0.0412	0.246	-548.9	0.00246	94.02
	15%	5.23	-627.0	0.0523	1.10	-945.7	0.0110	78.96
	25%	5.63	-741.8	0.0563	2.10	-762.5	0.0210	62.69

Polarization curves for Al/nano $(Al_2O_3)_p$ composites are shown in Figures (5) to (10). The Al/nano $(Al_2O_3)_p$ composites however, had better resistance to corrosion in Al – Fao water with inhibitor in comparison with the Al / nano $(Al_2O_3)_p$ composites without inhibitors.

This is an indication that the passive film formed on the surface of both the composites are stable and immune to attack when immersed in Al-Fao water

For all the investigated nanocomposites, there is a trend of increasing of the corrosion rate with the increase of the Al_2O_3 nanoparticulates weight percentage. The Al composite reinforced with 5% Al_2O_3 exhibited higher corrosion resistance with and without inhibitor and Al_2O_3 nanoparticulates are ceramic materials and they remain inert. The corrosion behavior of nanocomposites depends on weight percentage of the reinforcements.

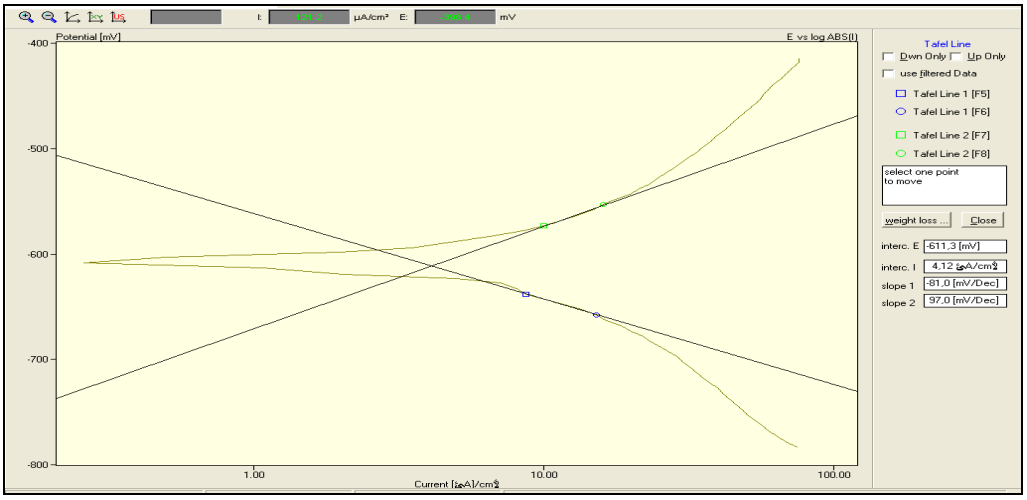


Figure (5) polarization curve for Al/ 5% nano Al_2O_3 composites without inhibitors

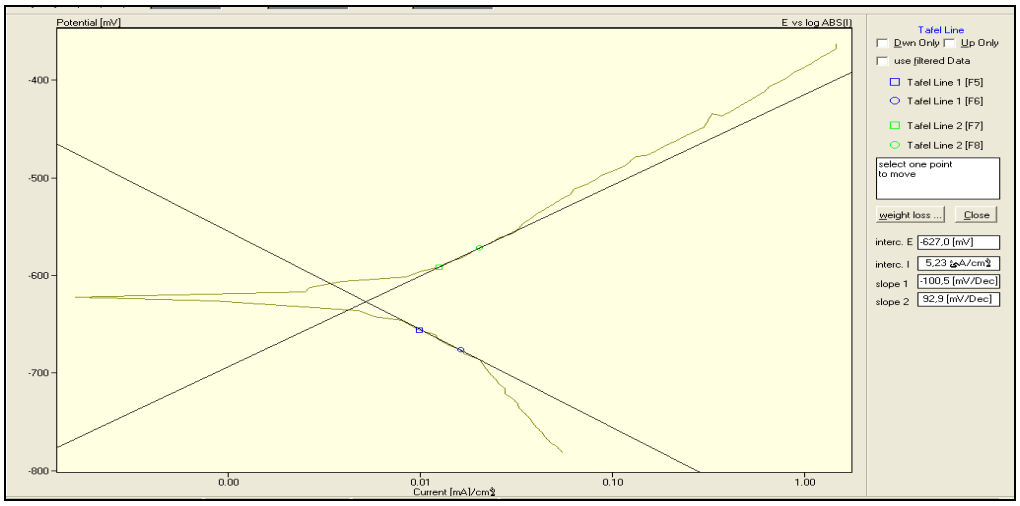


Figure (6) polarization curve for Al/15% nano Al_2O_3 composites without inhibitors

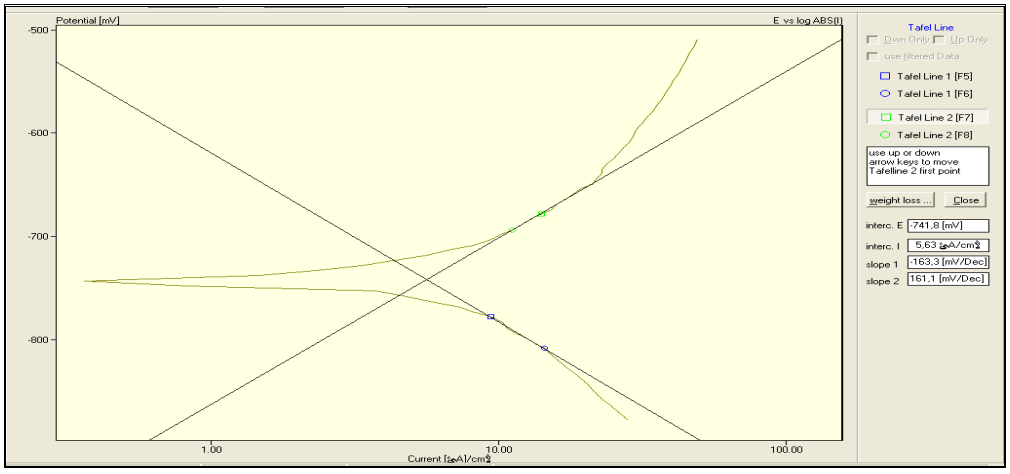


Figure (7) polarization curve for Al/25% nano Al_2O_3 composites without inhibitors

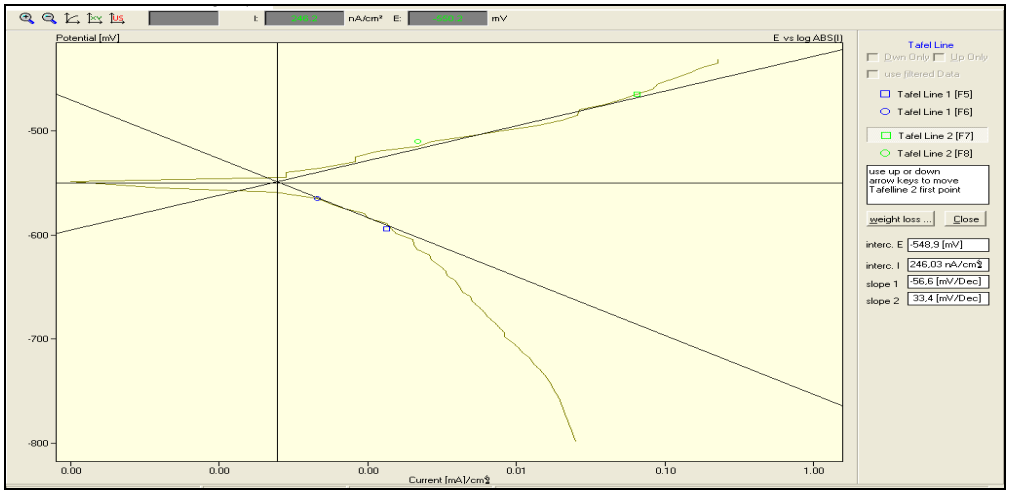


Figure (8) polarization curve for Al/5% nano Al_2O_3 composites with inhibitors

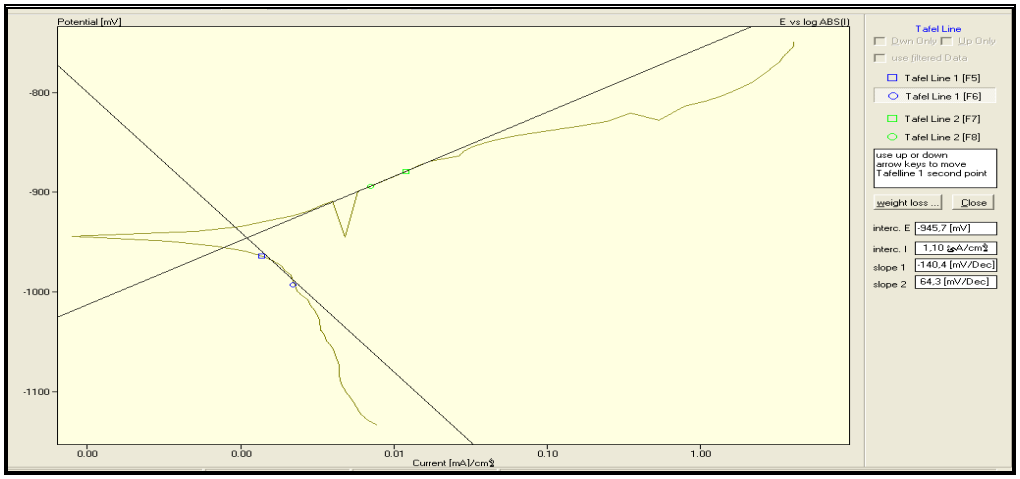


Figure (9) polarization curve for Al/15% nano Al_2O_3 composites with inhibitors

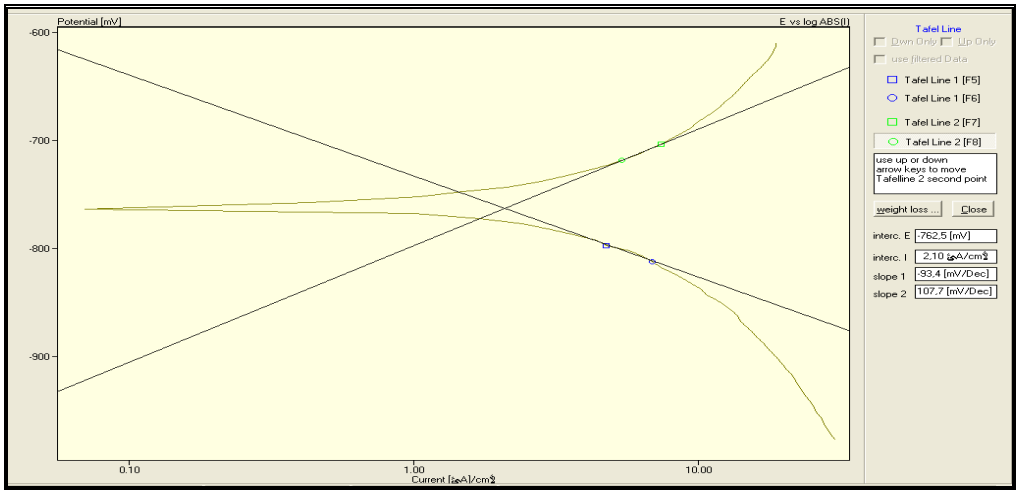


Figure (10) polarization curve for Al/25% nano Al_2O_3 composites with inhibitors.

FTIR Spectra :

The Fourier Transform Infrared spectroscopy is effectively used to identify the functional groups present in the synthesized compounds.

Closely related to adsorption studies of molecules by IR spectroscopy is the investigation of mechanisms of corrosion inhibitors IR- spectroscopy-based techniques in combination with electrochemistry have been used in a large number of studies to help elucidate the actual role of molecules that can act as corrosion inhibitors [11].

Characterization of the MMCs/liquid interface has traditionally been performed mainly through electrochemical techniques.

By integrating infrared reflection absorption spectroscopy into electrochemical measurements, it become possible to obtain atomic and information of adsorbents or films of reaction products on electrode surfaces in electrochemical environments.

Figure (11) shows the FTIR analysis of the Thiourea inhibitors which is used in the study.

The FTIR analysis was measured after immersion the MMCs samples for 15 days in Al-Fao water in case of absence of inhibitors. Figure (12) shows the results of FTIR spectrum of film formed on the Al/ Al_2O_3 MMCs surface after immersion in Al - Fao water in the presence of inhibitors The FTIR spectrum indicates appears many peaks, the most important peaks may be due to adsorption of compounds contained in Al-Fao water. Table (5) shows the IR band frequencies (cm^{-1}) of thiourea and of film formed on the Al/Al_2O_3 MMCs surfaces.

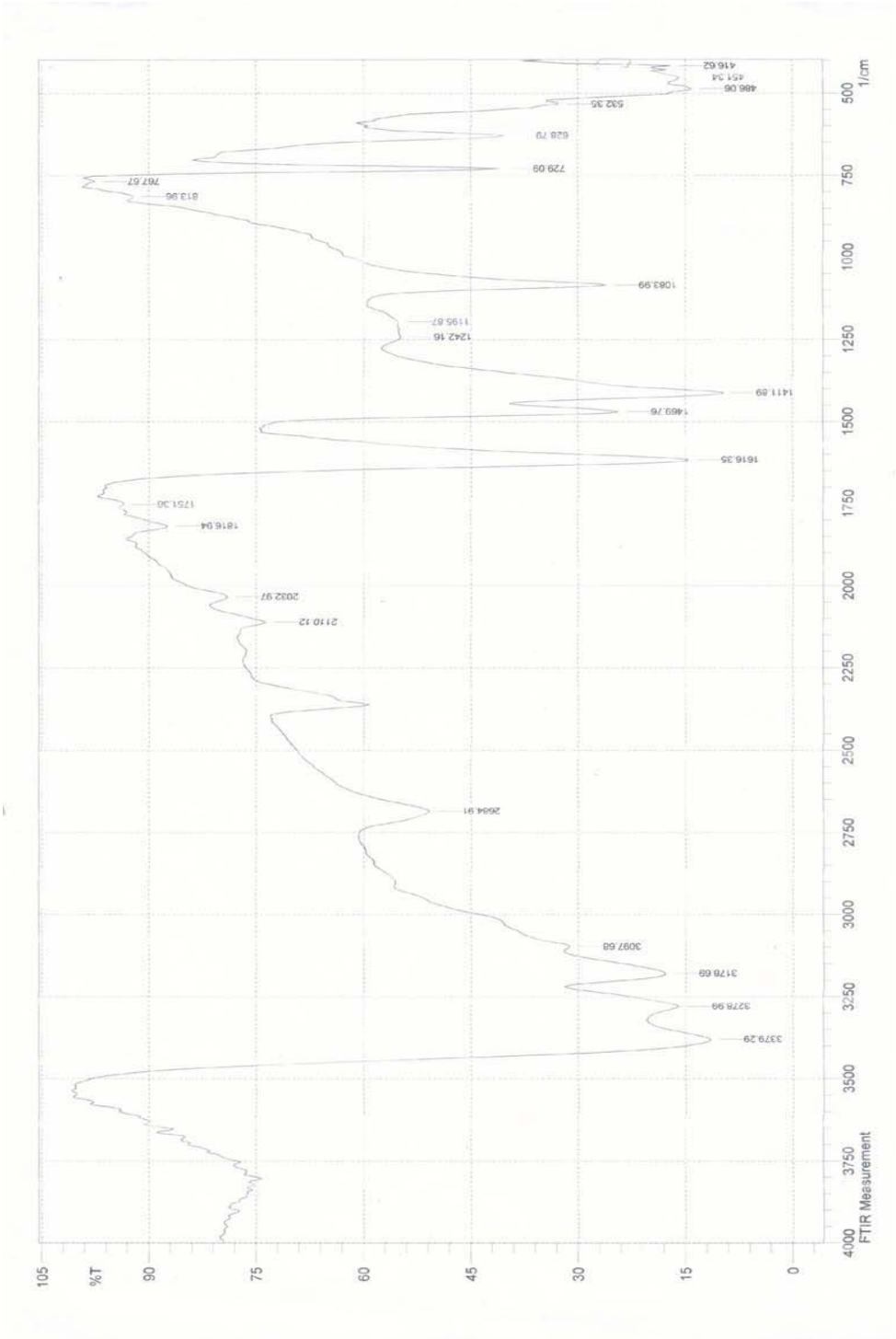
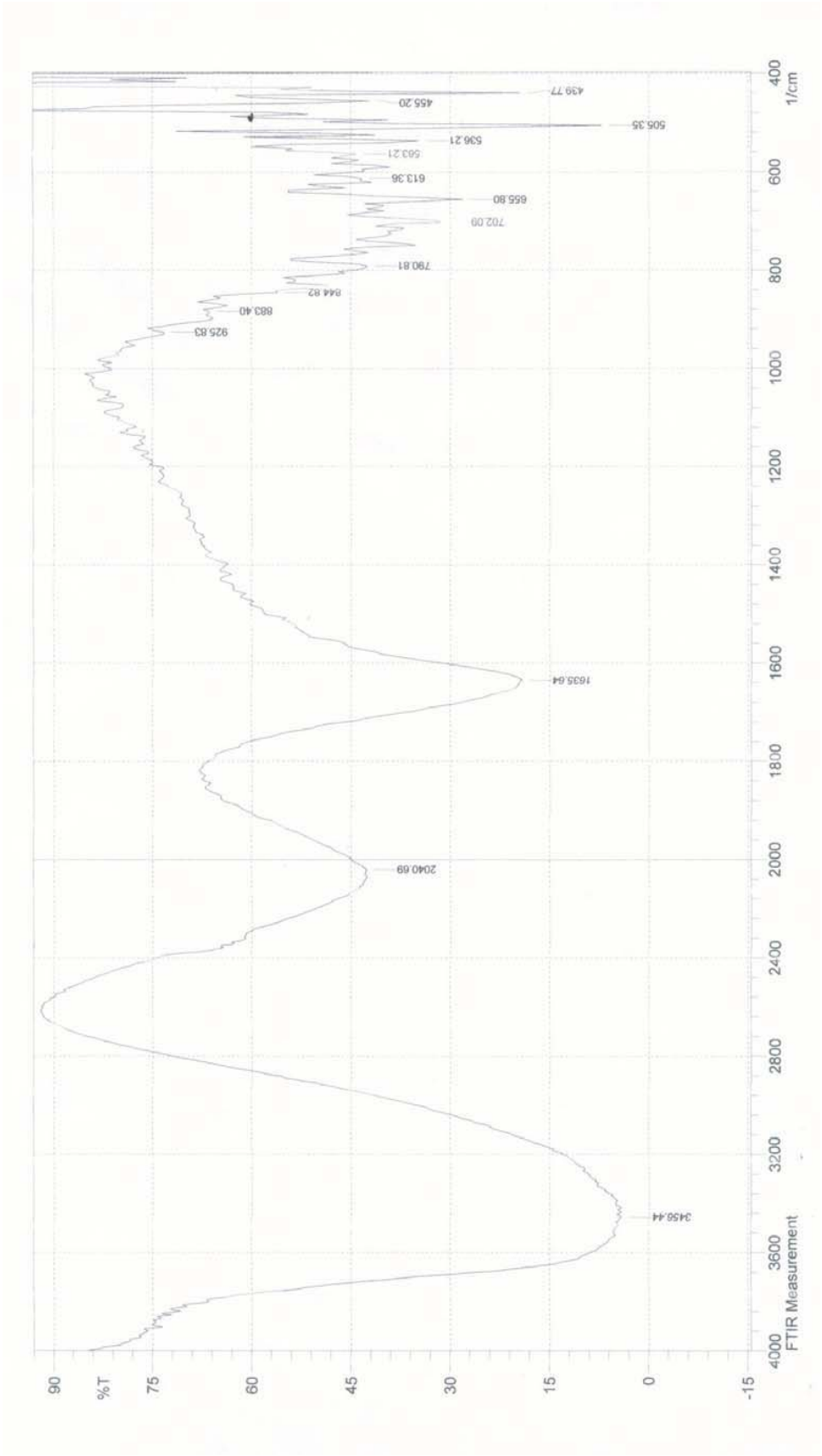


Figure (11) FTIR analysis of the Thiourea inhibitors which is used in this study.



Figures (12) FTIR spectrum of film formed on the Al/ Al_2O_3 MMCs surface after immersion in Al - Fao water in the presence of inhibitors

It has been indicated in the experimental part, thiourea contains some active groups such as the hydroxyl (OH) and the azo (N=N) groups. The presence of such groups may suggest the adsorption of these compounds on the aluminum MMCs surfaces. The adsorption may be physical or chemical using the lone pair of electrons present on the active groups. Upon the adsorption of these molecules on the electrode (MMCs), a surface layer is formed which obscures the part of metal surface beneath it. As a result, the MMCs surface becomes isolated from the corrosive medium and consequently the rate of corrosion is decreased.

Table (5) shows the IR band frequencies (cm^{-1}) of thiourea and the film formed on the Al/Al_2O_3 surfaces.

Thiourea (cm^{-1})	film formed on the Al/Al_2O_3 MMCs surfaces (cm^{-1})	Assignment
494	505.35	S-C-N symmetric bending
730	-	C=S stretching
1089	-	C=S stretching
1417	-	C=S asymmetric stretching
1627	1635.64	NH_2 bending
3379.29	3456.44	NH_2

Due to the double centers for thiourea, there is a possibility to coordinate with Aluminum in two ways i.e., through nitrogen or sulfur of thiourea. The high frequency N-H absorption bands in the region 3100 – 3400 cm^{-1} in the spectrum of thiourea have not been shifted to lower frequencies on the formation of metal thiourea complex which indicates that the bonding is only between sulfur and Aluminum atoms and not of nitrogen and Aluminum.

The symmetric bending S-C-N stretching vibrations at 494cm^{-1} of thiourea shifted to lower frequency at 448 cm^{-1} The symmetric and asymmetric C=S stretching vibrations at 730 and 1417 cm^{-1} of thiourea are shifted to low frequency region at 677 and 1403 cm^{-1} . C=S stretching vibration at 1089 cm^{-1} is shifted to higher frequency 1130 cm^{-1} shows the binding of Aluminum with thiourea is through sulphur. NH_2 bending at 1627 cm^{-1} is shifted to higher frequency region at 1644 cm^{-1}, asymmetric bending of NH_2 at 3376 cm^{-1} of thiourea shifted to lower frequency region at 3310 cm^{-1}.

CONCLUSIONS

According the results obtained from the current investigation, the following conclusions can be pointed out:

1. Thiourea acts as good corrosion inhibitors for MMCs in Al –Fao water.
2. The inhibition action of the thiourea against corrosion is due to the process of adsorption which is revealed by FTIR analysis.
3. Corrosion inhibition efficiency of thiourea increased with decreasing weight percentage of reinforcement for MMCs.
4. Small amount of inhibitor is given more efficiency.
5. The Al/ 5% Al2O3 nanocomposites exhibited the highest corrosion resistance among all the investigated composites.

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