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Corrosion Protection of Copper Using Azoles Applied on Its Surface at High Temperature Under Vacuum

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Application of seven different azoles namely; 1H-Pyrazole-3,5-diamine (azole 1), 1-Benzoyl benzotriazole (azole 2), 1-P-Chloro-Benzoyl benzotriazole (azole3), 1-P-Methoxy-Benzoyl benzotriazole (azole 4), 4-Phenyl-1H-pyrazole-3,5-diamine (azole5), N-[Benzotriazol-1-yl-(phenyl)-methylene]-N'-phenyl-hadrazine and 2-phenylbenzimidazole (azole 7) on the surface of copper at high temperature under vacuum was performed. The treated copper samples were subjected to corrosion testing in sulfide polluted salt water using potentiodynamic and potentiostatic techniques. The corroded samples were investigated using scanning electron microscope (SEM). The process was also applied for other metals (steel and aluminum) to address the specificity of the process.Potentiodynmaic polarization curves show that copper samples treated in the presence of the azole 6 exhibit extremely low passivation current ($<10^{-10}$ A cm^{-2}). Azoles 7,2 and 4 show low passivation currents ($<10^{-6}$ A cm^{-2}) while other azoles give high limiting currents ($>10^{-4}$ A cm^{-2}). It is also found that steel samples treated in the presence of azole (6) exhibit excellent corrosion protection while aluminum shows poor protection. Surface investigations supports the results of electrochemical tests. Results are discussed on the premise of the type of azole as well as the type of metal.

Keywords: Copper, corrosion inhibitors, pyrolysis, azoles

1. INTRODUCTION

Copper and copper alloys are widely used in industrial equipments. These alloys offer a particularly beneficial combination of electrical and/or thermal conductivity, corrosion resistance, strength and wear resistance. They are widely used for water cooling systems, desalination plants, shipboard condensers, power plant condensers and heat exchangers [1]. Copper and its alloys are subjected to corrosion in different environments; especially marine environments. The corrosion of copper and many of its alloys in marine environments has been extensively studied [2-8].

Benzotriazole ($C_6H_5N_3$, BTAH) and other azoles are the well known corrosion inhibitors of copper and many of its alloys. The excellent inhibiting efficiency of BTAH is attributed to the formation of a protective film of Cu(I)BTA on the copper surface [9-19]. Unfortunately benzotriazole loses its inhibition efficiency in environments polluted with sulfide ions. In such environments, sulfide ions compete for Cu(I) ions under a much stronger driving force than BTAH, consequently, sulfide ions can replace the Cu(I) ions in the Cu(I)BTA complex. This leads to the break down of the protective Cu(I)BTA film and occurrence of corrosion on the bare areas [19-21]. Until now, there are not known inhibitors which can resist the poisonous effect of sulfide ions

The present work addresses a new method of corrosion protection of copper which relies on the vacuum pyrolysis of azole inhibitors in the presence of copper samples. A protective layer of the inhibitor is expected to deposit on the surface of copper enhancing its corrosion resistance towards sulfide attack. In addition, the specificity of the method is also addressed through its application to metals other than copper.

2. EXPERIMENTAL

Electrodes were prepared from Cu (99.9 mass%) obtained from Goodfellow Corporation. Copper disc specimens of 1 cm diameter and 2 mm thickness were polished using SiC papers successively up to 2400 grits to acquire a mirror-like finish. A conventional three-electrode cell was used with a Ag/AgCl reference electrode, $E = 0.197$ V SHE, and a Pt sheet counter electrode. Solutions were prepared using double distilled water, Na_2S and NaCl were purchased from Fluka Chemicals.

Potentiodynamic polarization curves were measured on the Cu electrode in 3.5 mass% NaCl containing sodium sulfide at a voltage scan rate of 5 mV s^{-1}. The potential was controlled using a Gamry Instruments potentiostat which was also used in measuring potentiostatic polarization curves. Measurements were performed at $25^{o}C$ while the electrolyte was stirred using a magnetic stirrer. The surfaces of the electrodes were examined using JEOL Ltd., JSM- 6300 scanning electron microscope (SEM).

In the vacuum pyrolysis experiments, 3 polished specimens of copper were placed in a pyrex glass tube (15 mm diameter) together with about 0.3 g of the azole inhibitor. Seven different azoles were prepared as described previously [23]. The chemical structures of these azoles are illustrated in Table1. Once the azole inhibitor is placed inside the Pyrex tube the open part of the tube was narrowed to 3 mm diameter. The assembly was placed in liquid nitrogen to freeze the azole inhibitor inside and then connected to a vacuum pump which allows the pressure inside the tube to reach about 1.33 Pa. The tube was then sealed by heating its neck till melt and close. The tube is finally placed in the pyrolyser which adjusted to the desired temperature (150-350^{o}C). After vacuum pyrolysis for the desired time (30 min); the glass tube was broken and the copper specimens were taken out and corrosion tested. In most instances, both sides of copper specimens are covered with the inhibitor.

Under such condition, one side is repolished to make electrical connection through this side while the other side, covered with inhibitor, is exposed to the testing solution.

3. RESULTS AND DISCUSSION

Potentiodynamic polarization curves of copper samples treated in the presence of different azoles are shown in Fig.1.

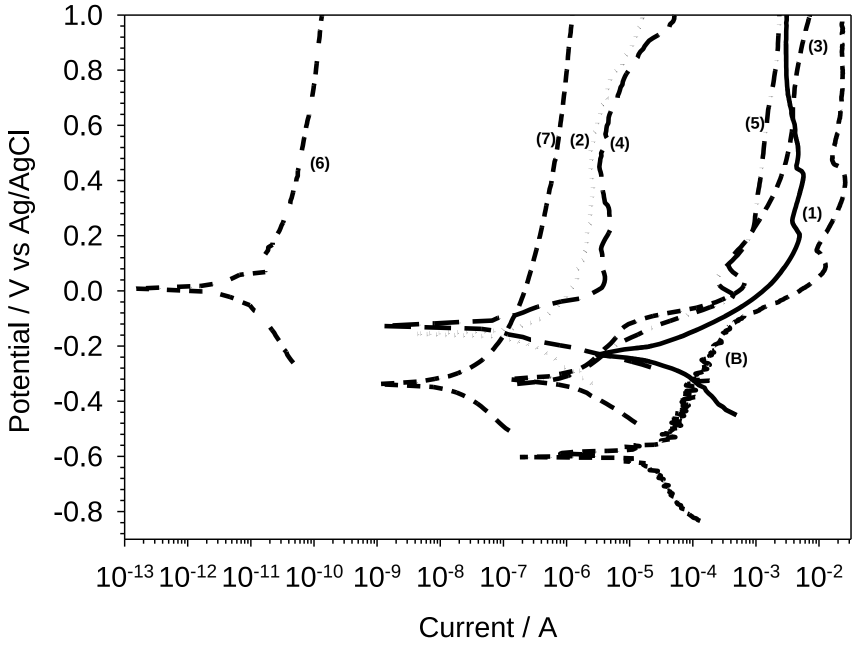
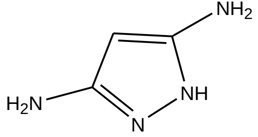
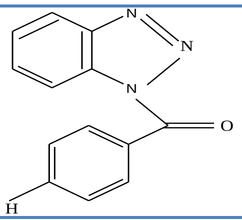
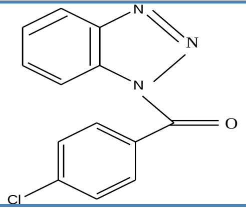
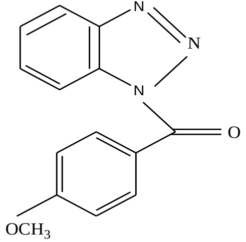
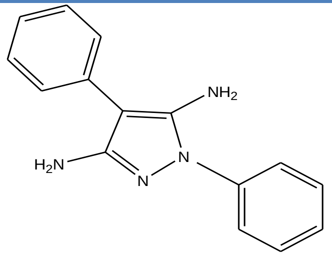
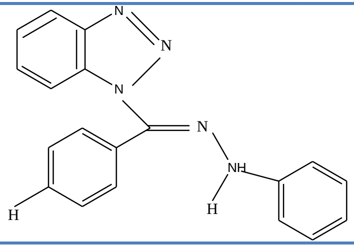
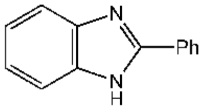


Figure 1. Potentiodynamic polarization curves of copper in 3.5% NaCl solution containing 0.001 M HS^- solution. Prior to testing, copper samples were treated in different azoles (1-7) as mentioned in Table 1. Curve B represents the untreated copper.

For the sake of comparison, the polarization curve of untreated copper is also included. The treatment of copper in the presence of different azoles leads to the shift in the corrosion potential (E_{corr}) in the noble direction towards more positive values. The highest shift in E_{corr} (~600 mV) is shown by azole (6) followed by azoles 2 and 4 (~500 mV) and then other azoles. The limiting currents shown by different azoles are also shifted towards lower values in comparison to that given by the untreated copper. Azole (6) gives an extremely low value of passivation current ($<10^{-10}$ A cm^{-2}) which is 8 orders of magnitude lower than the limiting current shown by the untreated copper (~10^{-2} A cm^{-2}). Azoles (7), (2) and (4) also give low passivation currents of 5.0×10^{-7}, 2.5×10^{-6} and 3.5×10^{-6} A cm^{-2}, respectively. Other azoles (1,3 and 5) give considerably high limiting currents ($>10^{-4}$ A cm^{-2}).

Table 1. Name, denoted name and the structure of the tested azole compounds. These compounds were pyrolyzed in the presence of copper samples under vacuum (1.33 Pascal) for 30 min at temperatures mentioned in the table.

Name	Denoted name	Structure	Treatment Temp. , ^{o}C
1H-Pyrazole-3,5-diamine	Azole (1)		250
1-Benzoyl benzotriazole	Azole (2)		200
1-P-Chloro-Benzoyl benzotriazole	Azole (3)		150
1-P-Methoxy-Benzoyl benzotriazole	Azole (4)		200
4-Phenyl-1H-pyrazole-3,5-diamine; compound with toluene	Azole (5)		175
N-[Benzotriazol-1-yl-(phenyl)-methylene]-N'-phenyl-hadrazine	Azole (6)		200
2-phenylbenzimidazole	Azole (7)		350

Potentiodynamic polarization curves were also used to deduce the corrosion parameters of copper namely; Corrosion potential (E_{cor}) corrosion current (I_{corr}) which in turn used to calculate the inhibitor (azole) percentage inhibition efficiency (E) according to the following equation [24]:

$$E = \frac{I_{corr\,(\mathrm{Blank})} - I_{corr\,(\mathrm{Azole})}}{I_{corr\,(\mathrm{Blank})}} \times 100 \qquad (1)$$

Table 2 summarizes the results. Low efficiency of 49% is shown by azole (1) while other azoles give very high inhibition efficiency (>90%). The highest inhibition efficiency (~100%) is shown by azole (6) and azole (7).

Table 2. Variation of corrosion parameters (corrosion current, I_{corr}, corrosion potential, E_{corr}, and percentage Inhibition Efficiency, *E*) of copper treated in the presence of different azoles. Treated copper specimens were tested in 3.5 mass% NaCl containing 0.001 mol L^{-1} sulfide ions.

	E_{corr} / V	I_{corr} / A	E (%)
Blank (Cu-only)	-0.83	3.83×10^{-5}	
Azole (1)	-0.23	1.96×10^{-5}	48.83
Azole (2)	-0.16	4.44×10^{-7}	98.84
Azole (3)	-0.32	1.70×10^{-6}	95.56
Azole (4)	-0.09	2.33×10^{-6}	93.91
Azole (5)	-0.34	7.54×10^{-7}	98.03
Azole (6)	-0.013	1.57×10^{-11}	99.99
Azole (7)	-0.34	7.91×10^{-8}	99.79

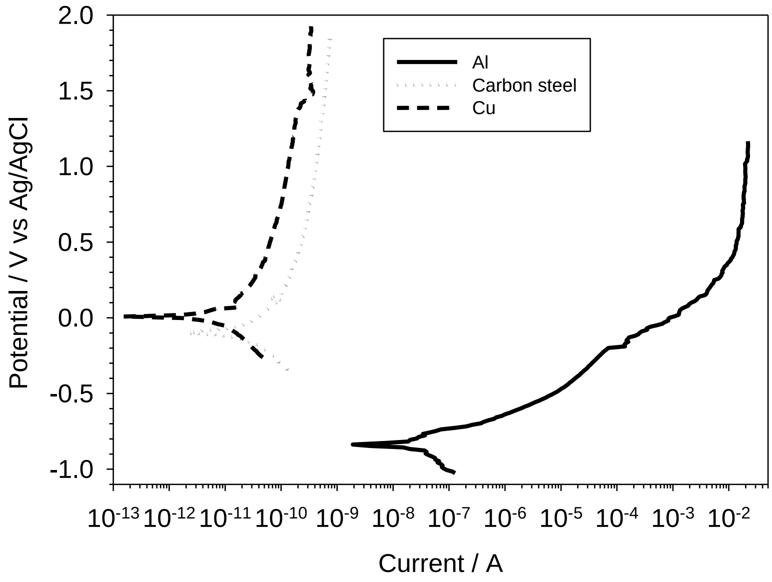


Figure 2. Potentiodynamic polarization curves of Cu, Al and carbon steel in 0.001 M sulfide polluted salt water. Prior to testing, metals were treated in Azole (6) for 30 min at 200°C under vacuum.

Fig.2 shows the potentiodynamic polarization curves of copper, aluminum and steel after treatment for 30 min at 200°C under vacuum in the presence of Azole (6). The application of azole (6) under the afore mentioned conditions exerts excellent corrosion resistance on the surface of steel towards sulfide attack. A very low passive current of 10^{-9} A is obtained. On the other hand, treatment of aluminum under the same conditions exerts no improvement on its corrosion resistance. A limiting current of about 10^{-4} A is obtained. These results suggest that the treatment process is applicable for some metals but not others.

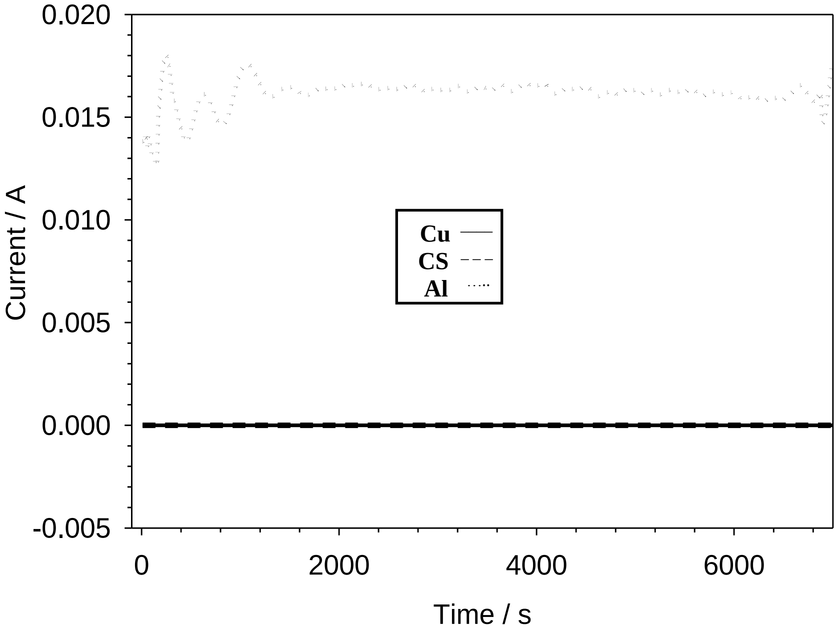


Figure 3. Potentiostatic polarization curves of Cu, Al and carbon steel in 3.5% NaCl containing 0.001 M sulfide ions at 0.5 V (Ag/AgCl). Prior to testing, metals were treated in Azole (6) for 30 min at 200°C under vacuum.

Fig.3 shows the potentiostatic polarization curves of copper, steel and aluminum samples tested at 0.5 V (Ag/AgCl) in 0.001 M sulfide polluted salt water. Prior to testing, samples were pretreated in the presence of azole (6) at 200°C under vacuum for 30 min as previously described. The results of potentiostatic experiments support those of potentiodynamic tests. Copper and steel show extremely low steady state currents ($<10^{-9}$ A cm^{-2}) while aluminum sample shows a high steady current of 1.7×10^{-3} A cm^{-2}.

3.1. Surface characterization

Fig. 4 illustrates cross sections of copper, steel and aluminium samples subjected to vacuum pyrolysis in the presence of Azole (6). Images differentiate two distinct layers; one represents the metal while the other represents a compact layer of the inhibitor deposited on the metal surface. SEM images show clear differences between the inhibitor layers deposited on different metals. In case of copper the deposited layer was thick reaching 128 µm. The deposited layers on steel and aluminum show quite small thicknesses of 5 and 8 µm, respectively. These values are quite low in comparison to that shown by copper. The difference between deposited layers on steel and aluminium is that; the layer deposited on steel is homogeneous while that deposited on aluminum is irregular.

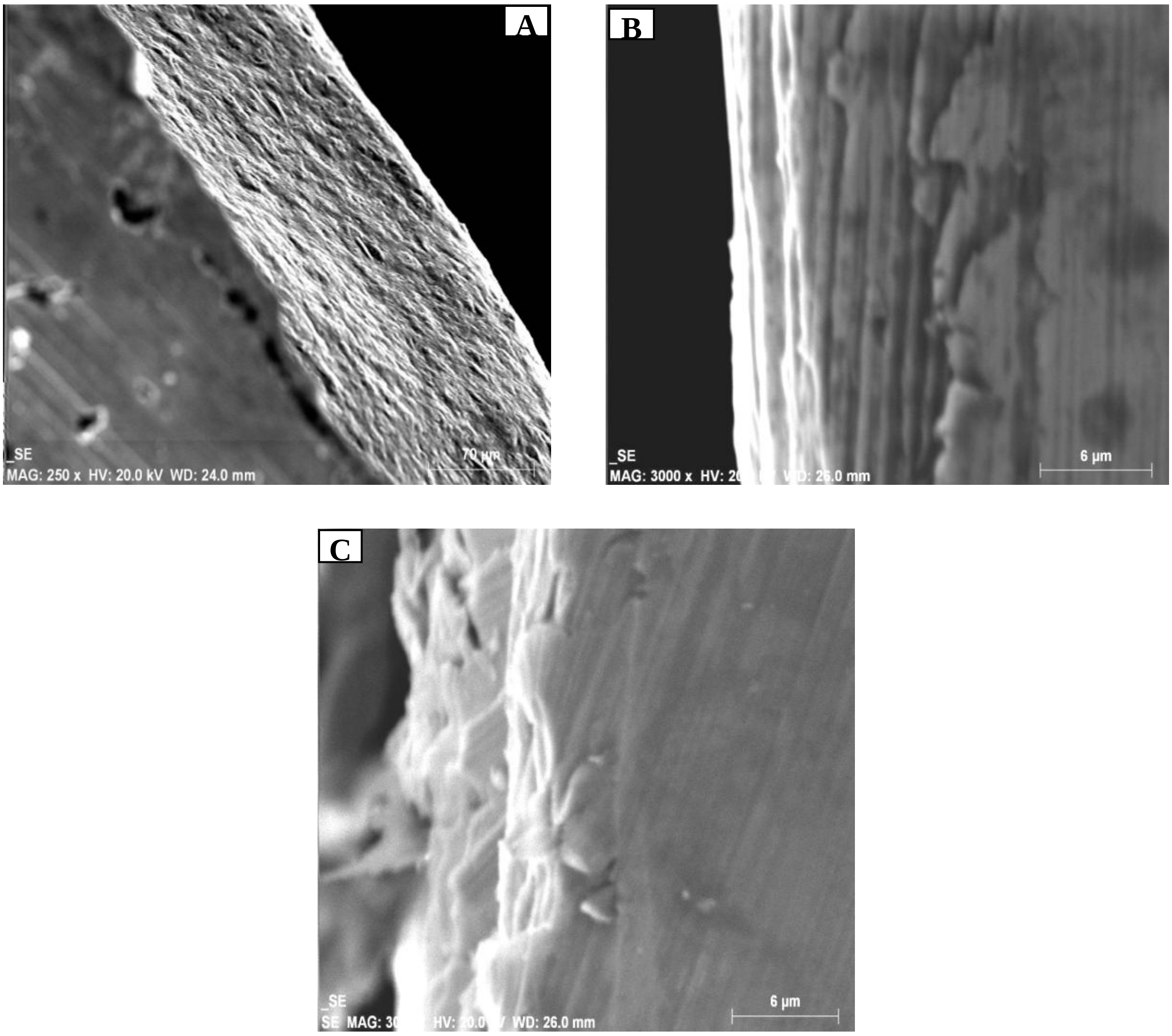


Figure 4. SEM micrograph of the cross sectional area of copper (a), carbon steel (b) and aluminum (c) treated in Azole (6) for 30 min at 200°C under vacuum.

Fig. 5 shows the surface of copper, steel and aluminum potentiostated in 0.001 mol L^{-1} sulfide polluted salt water after removal of the deposited layer of Azole (6). The surfaces of both copper and steel show very good appearance with no corrosion attack. On the other hand, the surface of aluminium sample shows severe corrosion attack.

Surface investigations revealed that the deposited inhibitor layer is distinct and differentiated from the metal surface. This observation suggests that there is no chemical interaction between the metal and the inhibitor and consequently look to the vacuum pyrolyisis of azoles as a kind of coating rather than chemisorption. The process looks like hot-melt dip coating. When azole reaches a temperature higher than its melting point it transfers into liquid which spreads and adheres to the surface of copper.

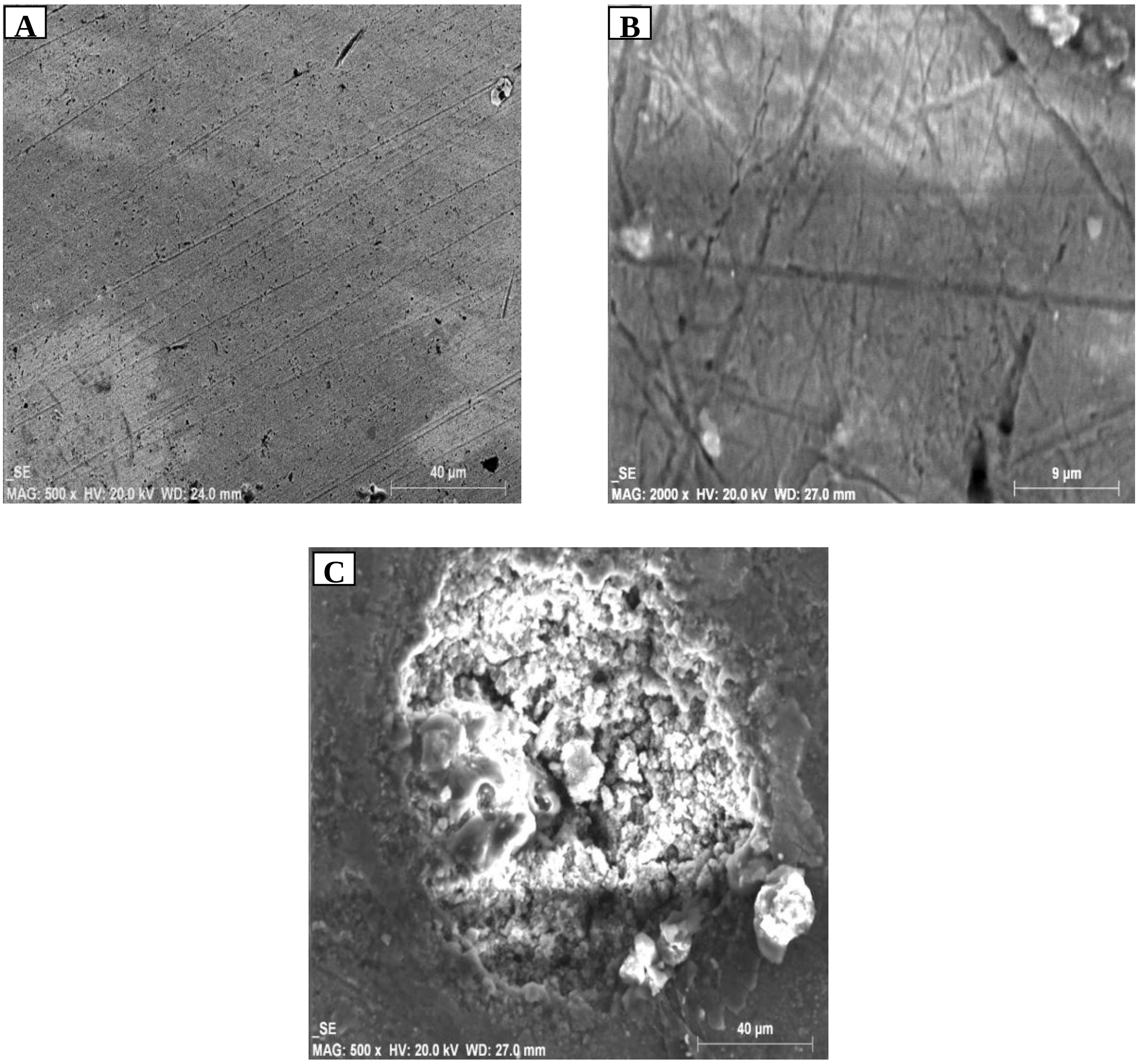


Figure 5. SEM micrographs of the surface of copper (a), carbon steel (b) and luminum (c) after potentiostatic testing (see Fig. 3) of metal samples that were treated in Azole (6) for 30 min at 200^{o}C under vacuum. Prior to SEM investigation the deposited layer of Azole (6) was removed.

The adhered layer behaves like a barrier hydrophobic coating that effectively prevent electrolyte from contacting the metal surface and excellently resist corrosion attack. The difference in efficiency between different azoles can be related to the properties of the formed barrier coating. Low efficient azoles form coating layers either do not well adhered to the metal surface or have some degree of porosity which allows the electrolyte to penetrate the coat and attack the metal surface. Highly efficient azoles, especially azole (6), form barrier coatings which act as perfect insulators preventing the penetration of the electrolyte. The deposited layer on steel and aluminum are of quite low thickness compared to that of copper. However; the layer deposited on the steel surface was highly protective while that deposited on the aluminum surface was unprotective. This can be related to the fact that the deposited layer on steel is homogeneous and compact while that deposited on aluminum is irregular and not well adhered. The proposed method is proofed to be applicable for some metals but not the others. This can be related to the wetting ability of the metal towards the coating substance.

4. CONCLUSIONS

The present work shows that vacuum pyrolysis of azoles on copper leads to the deposition of a compact layer of the inhibitor on the copper surface. The deposited layer impairs very high inhibition efficiency on the copper surface towards sulfide attack. The proposed method was shown to be very effective upon application on copper and steel surfaces but failed to protect aluminum surface.

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