

Comparative analysis of the corrosion resistance of Bos taurus and Cocos nucifera reinforced 1170 aluminium alloy in chloride-sulphate solution

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Abstract

Reinforced AA1170 aluminium alloy with particulates of *Bos taurus* (BT) and *Cocos nucifera* (CN) (0% to 20% wt. concentration) was evaluated for their corrosion resistance properties in 3.5% NaCl and 0.05 M H_2SO_4 solution by potentiodynamic polarization, open circuit potential analysis, potentiostatic analysis, optical and scanning electron microscopy and x-ray diffractometry. Results showed corrosion rate of monolithic aluminium alloy (0% particulate wt. concentration) from both electrolytes (3.5% NaCl and 0.05 M H_2SO_4) are 0.204 and 0.259 mm/y. Corrosion rate of BT reinforced composites from both solutions decreased with respect to BT particulate concentration to 0.087 and 0.216 mm/y at 20% BT. Whereas corrosion rate of CN reinforced composites decreased to 0.161 mm/y in 3.5% NaCl and increased to 0.434 mm/y in 0.05 M H_2SO_4 at 20% CN concentration. The most passivated aluminium composites from polarization plots occurred 5% BT and CN particulate concentrations. Increase in particulate concentration results in vulnerability to localized corrosion. Open circuit potential plots show the presence of the particulate reinforcements increased the thermodynamic instability of the surface properties of the composite and its exposure to active-passive transition behavior. Optical and scanning electron microscopy indicates significant improvements in the corrosion resistance of BT and CN particle reinforced aluminium compared to the unreinforced alloy were significant surface deterioration, pitting corrosion and intergranular corrosion were presence. X-ray diffractometry showed the phases identified for BT particle reinforced composite (Al_2O_3 , Cu_5S_2 , Zn_5S_2 , ZnCO_3 and CuO_2) significantly enhances its corrosion resistance compared to the monolithic and CN particle reinforced composite.

Introduction

Metal matrix materials have gained global attention due to their unique metallurgical, mechanical and corrosion resistance properties compared to traditional metallic alloys. They are at the forefront of probable competitors for advanced engineering applications [1]. Their application is basically structural; extending across automobile, aerospace, shipping and marine, energy generation, desalination, construction, defense and space exploration industries due to their higher strength-weight ratio, moderate density and coefficient of thermal expansion, enhanced mechanical properties, high specific strength and stiffness, and electrical conductivity [2–6]. Aluminium is the most copious metal in the Earth's crust, constituting about 8% of the earth's crust. Aluminium matrix composites consist of the admixture of two or more reinforcements added to the base aluminium metal. The properties of aluminium matrix composites can be modified to suit the requirements of various industrial establishments by proper combinations of matrix, reinforcement and processing method [7, 8]. The reinforcements are usually particulates, whiskers and fibers within the microstructure of the aluminium alloy resulting in improved engineering materials [9]. Particulate reinforced metal matrix composites usually contain ceramic reinforcements e.g. Al_2O_3 , SiC, TiB_2 , TiC etc. with volume fraction not more than 30%. Though SiC and Al_2O_3 are mostly used [10]. They are usually produced by the admixture of the base aluminium and the particulate powders prior to stir casting liquid-metal techniques for the manufacture of components for automotive, aerospace and energy applications. Stir casting is a cost-effective technique for the

production of metal matrix composites due to its versatility, relative cost, and volume space [11, 12]. The general production output of the matrix composites is a product of the type of reinforcement and its bond strength. However, reinforced particles are responsible for inhomogeneities on the microstructure of the matrix composites which invariably exposes them to corrosion. Currently, replacement of ceramic reinforcements in aluminium matrix composites with sustainable waste products especially agricultural waste is ongoing [13]. Although non-degradable industrial waste (quarry dust spent catalyst, fly ash, and red mud) have also been used in aluminum matrix [14]. Agricultural wastes ash from rice husk, snail shell, maize husk, coconut shell, eggshell, bamboo leave etc., have been successfully used as reinforcement in aluminium matrix composites [15]. Their ready availability, recyclability, cost and renewability in abundance inevitably leads to cheaper source of reinforcement for aluminium. Aluminium matrix composites exhibits numerous advantages compared to their monolithic counterparts as earlier mentioned. However, they can be prone to corrosion attack. Corrosion is the degradation metallic and non-metallic materials due to electrochemical interaction with their operating environment. There are different methods of controlling corrosion including the versatile method corrosion inhibitor application [16–18]. Research on the corrosion resistance properties of aluminium matrix composites is also ongoing, though findings have shown that reinforcements influences the localized corrosion resistance of the composites [19, 20]. Hemanth and Divya [21] studied the corrosion resistance of aluminum alloy reinforced with Nano-ZrO₂. Result showed the corrosion resistance of the composite increased with increase in ZrO₂ content. Kumar *et al* [22] studied the corrosion resistance of aluminium-SiC matrix composite with the Taguchi based grey relation analysis in 3% NaCl solution. Results showed according to F value that the vol. % of SiCp on the composite, extent of immersion time in 3% NaCl solution and aging significantly influenced the corrosion rate of the composite. Loto and Adeleke [23] studied the electrochemical behavior of aluminium-SiC composite in chloride solution. Results showed the unreinforced aluminium alloys exhibited lower corrosion rates compared to the aluminium composite. Localized corrosion was also observed. Deshpande *et al* [24] investigated the corrosion resistance of carbon fiber reinforced aluminium composite in 3.5 wt.% aqueous NaCl solution. Data obtained showed the corrosion potentials shifted negatively coupled with increase in corrosion current density as a result of galvanic coupling between carbon fiber and matrix. Flachmann *et al* [25] investigated the corrosion resistance of Al₂O₃ particle reinforced aluminium composite in chloride solution through immersion test. Corrosion rate data and microstructural characterization images indicates accelerated corrosion specifically intergranular corrosion. Corrosion occurs mainly at the reinforcement/metal interface, along grain boundaries and in the form of pits [26, 27]. In contribution to the research on corrosion resistance of aluminium matrix composites, this manuscript investigates and compares the corrosion resistance of *Cocos nucifera* and *Bos taurus* ash reinforcements within aluminium matrix composites in neutral chloride and acid chloride solutions.

Experimental methods

Materials and preparation

AA1170 aluminium alloy (A-70) with radial proportions of 2.6 cm was split into 5 workpieces having square proportions of 1 cm by 2 cm using manual hand tool for potentiostatic analysis and open circuit potential evaluation. Elemental analysis of the Al work piece with PhenomWorld high resolution electron microscope was carried out at Covenant University Central Instrumentation Research Facility, Ota, Ogun State, Nigeria. The %wt. composition of A-70 is shown in Table 1. Cu cables were affixed to A-70 work pieces with soft solder before being enmeshed pre-solidified acrylic paste. The exterior area of the A-70 work piece was graded with emery sheets (60–1500 grits), brightened with 3 µm diamond mixture and washed with de-mineralized H₂O and dimethylketone. *Cocos nucifera* shells (CN) obtained from the local market and *Bos taurus* bones (BT) obtained from the local abattoir were dried for two weeks. BT was burnt at a fixed temperature of 900°C and subsequently grinded to powdery form [28]. CN was processed in accordance with [29], until a powdery form was achieved. Stir casting method was used to melt A-70 (approx. 45 min at 660 °C). CN and BT were added to A-70 melt in wt.% of 5%, 10%, 15% and 20% and subsequently casted and cooled for 24 h. A-70/BT and A-/CN casts with respect to wt.% composition were thereafter cut with power hacksaw into proportions of 1 cm by 1 cm by 1 cm and added to the prepared electrolytes. Table 2 shows the designation of A-70 with respect to BT and CN particulate wt.% composition. 0.05 M H₂SO₄ solution was concocted from standard class H₂SO₄ acid solution. NaCl solution at 3.5% concentration was prepared from recrystallized NaCl. A third solution consisting of admixed 0.05 M H₂SO₄ and 3.5% NaCl solution was also prepared.

Table 1
Elemental composition (wt.%) of A-70 workpiece

Element	Fe	Si	Cu	Zn	Ti	Mg	Pb	Sn	Al
%wt. Composition	0.232	0.078	0.0006	0.0016	0.006	0.0027	0.0012	0.007	99.66

Table 2
Designation of A-70 with respect to BT and CN particulate wt.% composition

Work Pieces	Designation System	BT wt.%	Work Pieces	Designation System	CN wt.%
AB	A-70	0	AB	A-70	0
A2	A-70/5%	5	B2	A-70/5%	5
A3	A-70/5%	5	B3	A-70/5%	5
A4	A-70/15%	15	B4	A-70/15%	15
A5	A-70/15%	15	B5	A-70/15%	15

Potentiodynamic polarization and open circuit potential evaluation

Corrosion kinetics was evaluated with potentiodynamic polarization method while corrosion thermodynamics was determined by open circuit potential analysis. Both test was done at 308 K (ambient temperature) by adopting a Digi-Ivy 2311 potentiostatic apparatus. The apparatus consisting of a triple cord electrode (A-70 workpiece electrode, Ag/AgCl threshold electrode and Pt cord counter electrode) was networked to a laptop computer, Polarization data lines were drawn at plot progression of 0.0015 V/s initiating at -1.75 V to + 2 V. Corrosion potential, C_p (V) and Corrosion current density C_j , (A/cm^2) results were acquired by Tafel computation. Corrosion rate, C_r (mm/y) was quantified from the numerical formulae below;

$$C_{RT} = \frac{0.00327 C_J C_q}{D} \quad (1)$$

E_w indicates equivalent weight (g) of A-70, 0.00327 indicates corrosion constant while D indicates density (g/cm^3). Polarization resistance, P_{rt} (Ω) was assessed from the numerical formulae below;

$$P_{rt} = 2.303 \frac{B_a B_c}{B_a + B_c} \left(\frac{1}{I_{cr}} \right) \quad (2)$$

B_a and B_c indicates anodic and cathodic Tafel slopes (V/dec).

Scanning electron microscopy, X-ray Diffractometry and X-ray Fluorescence

Scanning electron microscopic images (mag. x500 and x1000) of A-70 work piece were obtained using PhenomWorld scanning electron microscope prior to and following corrosion test at specific NaCl, H_2SO_4 and NaCl/ H_2SO_4 solution. X-ray diffraction data and information on the component phases, compounds, impurities, precipitates etc. on A-70 work piece were obtained after scanning with Rigaku D/Max-IIIc X-ray diffractometer at sweep rate of $2^\circ/min$ within 2 to 50° at ambient temperature with a Cu K-alpha radiation established at 40kV and 20mA in 2θ . The diffraction results (correlation magnitude) received was compared to threshold results obtained from mineral powder diffraction folder (ICDD) containing the threshold information of over 3000 minerals. The composition of A-70 surface and its corroded specimens was evaluated using Lab-X3500 Benchtop XRF Analyser with detection limits at ppm to 100%. The Lab-X 3500 instruments are fitted with Oxford Instruments Analytical Software Package, ASP3500 and pre-defined calibrations.

Potentiodynamic polarization studies

Graphical representations of the corrosion polarization curves for sample AB, samples A2 to A5, and samples B2 to B5 aluminium matrix composites from 3.5% NaCl are show in Fig. 1a and 1b. The corresponding polarization curves for the composites in 0.05 M H_2SO_4 solution are shown in Fig. 2a and

2b. Table 3 shows the polarization data for sample AB, samples A2 to A5, and samples B2 to B5 aluminium matrix composites from 3.5% NaCl while Table 4 shows the corresponding data for the composites from 0.05 M H₂SO₄ solution. The corrosion rate results in Table 3 shows progressive decrease in value with respect to BT concentration compared to the corresponding corrosion rate values of the composites with respect to CN concentration in NaCl solution where increase in corrosion rate values was observed. Corrosion rate of the composites (with respect to BT particulate concentration) in NaCl solution initiated at 0.204 mm/y (0% BT concentration) corresponding to corrosion current density of 1.85×10^{-5} A/cm² and polarization resistance of 1386 Ω, and progressively decreased to 0.087 mm/y (corrosion current density of 7.87×10^{-6} A/cm² and polarization resistance of 3266 Ω) at 20% BT concentration. The corrosion rate values of the composites with respect to CN concentration decreased to 0.093 mm/y (8.45×10^{-6} A/cm² and 3043 Ω) at 5% CN concentration before progressively increasing to 0.161 mm/y (1.46×10^{-5} A/cm² and 1755 Ω) at 20% CN concentration. These observations are due to differences in the resulting microstructural properties of the composites with respect to BT and CN particulate reinforcements. In the presence of Cl⁻ anions the ability of the composites to repair their passive protective oxide is greatly influenced by the reinforcements and the reactive tendency of the Cl⁻ anion to aggravate the evolution and progression of localized corrosion [30–34]. Decrease in corrosion rate values of the composites in the presence of BT reinforcements shows galvanic effect between the reinforcement and aluminium substrate metal is limited coupled with limited localized corrosion in the form of corrosion pits and along the grain boundary. The size of Cl⁻ anions allows for diffusion through the protective oxide on the composite. This is evident by the increase in corrosion rate results for the composite in the presence of CN particulate where increase in Cl⁻ anion concentration results in greater diffusion of the anion and inability of the protective oxide to repassivate [35].

Corrosion rate values of the BT and CN particle reinforced composites in Table 4 are generally higher in 0.05 M H₂SO₄ solution compared to 3.5% NaCl solution due to the higher dissociation constant and acidity of the sulphate species. Corrosion rate of BT reinforced composite initiated at 0.259 mm/y (corrosion current density of 2.36×10^{-5} A/cm² and polarization resistance of 1090 Ω) at 0% BT concentration before increasing sharply to 0.534 mm/y at 5% BT concentration. Beyond this concentration corrosion rate value progressive decreased with increase in BT concentration, culminating at 0.216 mm/y (1.96×10^{-5} A/cm² and 1309 Ω) at 20% BT concentration. This shows increase in BT concentration visibly reduces the corrosion rate of BT reinforced aluminium matrix composites. This observation differs from the corrosion rate data obtained for CN reinforced matrix composites where the corrosion rate increased significantly with increase in CN concentration. Corrosion rate at 5% CN concentration is 0.290 mm/y corresponding to corrosion current density of 2.64×10^{-5} A/cm² and polarization resistance of 1262 Ω. At 20% CN concentration, corrosion rate has increased to 0.434 mm/y (corrosion current density of 3.94×10^{-5} A/cm² and polarization resistance of 651 Ω). The trend in corrosion rate values for BT and CN particle reinforced matrix composites is similar to the trend observed for the corrosion rate values obtained from the neutral chloride solution. This phenomenon as earlier

explained is due to differences in the metallurgical structure of the matrix composites and by extension their microstructural properties.

Observation of the anodic-cathodic plots in Fig. 1a and 1b shows significant passivation of the polarization plots especially at 0% and 5% particulate concentrations of BT and CN. Beyond these concentrations the passivation characteristics of the polarization plots decreased. Passivation of the matrix composites in the presence of SO_4^{2-} anions occurred as shown in Fig. 2a and 2b, however to a lesser degree due to the mechanism of electrochemical deterioration in the presence of the SO_4^{2-} anions. Variation of the corrosion potential of the polarization plots in Fig. 1a shows significant transition between anodic and cathodic potentials. The corrosion potential of -1.094 V at 0% BT concentration shifted to -1.107 V at 5% BT concentration, after which variation in the cathodic direction to -0.994 V at 20% BT concentration dominated the reaction processes. This shows cathodic reaction process associated with H_2 evolution and O_2 reduction were dominant. This observation shows localized corrosion is more evident and is the mechanism of deterioration of the microstructural properties of the composite in NaCl solution. The corrosion potential of the polarization plots in Fig. 1b shifted anodically from -1.094 V at 0% CN particulate concentration to -0.936 V at 15% CN particulate concentration. This indicates the effect of the surface oxide properties on the reaction mechanism in the presence of CN particulate and the subsequent oxidation of the composite surface. Beyond 15% BT particulate concentration, cathodic potential shift occurred till -1.068 V at 20% CN particulate concentration. The corresponding corrosion potential values in Fig. 2b varied instantaneously between anodic and cathodic potentials with respect to CN particulate concentration. The analogous corrosion rate values indicate severe surface degradation as the particulate concentration increases. Whereas, the corrosion potential values in Fig. 2b shifted in the anodic direction after 0% BT particulate concentration from -0.630 V at 5% BT particulate concentration to -0.579 V. Comparing the values with the corrosion rate data, it is evident that increase in BT particulate concentration significantly influenced the formation of protective oxide on the composite surface simultaneously with the oxidation/corrosion of the composite surface.

Table 3

Potentiodynamic polarization data for BT and CN aluminium matrix composites from 3.5% NaCl solution

BT Particle Reinforced Aluminium Matrix Composite							
BT Conc. (%)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm ²)	Corrosion Potential (V)	Polarization Resistance, R_p (Ω)	Cathodic Tafel Slope, B_c (V/dec)	Anodic Tafel Slope, B_a (V/dec)
0	0.204	1.85×10^{-5}	1.85×10^{-5}	-1.094	1386.00	-9.828	3.433
5	0.182	1.65×10^{-5}	1.65×10^{-5}	-1.107	1425.00	-8.909	3.084
10	0.154	1.40×10^{-5}	1.40×10^{-5}	-0.965	1842.00	-9.001	5.615
15	0.122	1.11×10^{-5}	1.11×10^{-5}	-0.992	2319.00	-8.902	3.622
20	0.087	7.87×10^{-6}	7.87×10^{-6}	-0.994	3266.00	-9.431	3.172
CN Particle Reinforced Aluminium Matrix Composite							
CN Conc. (%)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm ²)	Corrosion Potential (V)	Polarization Resistance, R_p (Ω)	Cathodic Tafel Slope, B_c (V/dec)	Anodic Tafel Slope, B_a (V/dec)
0	0.204	1.85×10^{-5}	1.85×10^{-5}	-1.094	1386.00	-9.828	3.433
5	0.093	8.45×10^{-6}	8.45×10^{-6}	-0.948	3043.00	-8.577	4.043
10	0.107	9.70×10^{-6}	9.70×10^{-6}	-0.936	2862.00	-9.434	1.356
15	0.120	1.09×10^{-5}	1.09×10^{-5}	-0.972	2356.00	-9.531	3.998
20	0.161	1.46×10^{-5}	1.46×10^{-5}	-1.068	1755.00	-8.994	3.284

Table 4
Potentiodynamic polarization data for BT and CN aluminium matrix composites from 0.05 M H₂SO₄ solution

BT Particle Reinforced Aluminium Matrix Composite							
BT Conc. (%)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm ²)	Corrosion Potential (V)	Polarization Resistance, R_p (Ω)	Cathodic Tafel Slope, B_c (V/dec)	Anodic Tafel Slope, B_a (V/dec)
0	0.259	2.36×10^{-5}	2.36×10^{-5}	-0.613	1090.00	-9.103	3.943
5	0.534	4.85×10^{-5}	4.85×10^{-5}	-0.630	439.00	-8.010	4.074
10	0.356	3.24×10^{-5}	3.24×10^{-5}	-0.600	794.40	-9.046	3.797
15	0.275	2.50×10^{-5}	2.50×10^{-5}	-0.592	1160.00	-8.268	6.155
20	0.216	1.96×10^{-5}	1.96×10^{-5}	-0.579	1309.00	-8.353	4.275
CN Particle Reinforced Aluminium Matrix Composite							
CN Conc. (%)	Corrosion Rate (mm/y)	Corrosion Current (A)	Corrosion Current Density (A/cm ²)	Corrosion Potential (V)	Polarization Resistance, R_p	Cathodic Tafel Slope (B_c)	Anodic Tafel Slope (B_a)
0	0.259	2.36×10^{-5}	2.36×10^{-5}	-0.613	1090.00	-9.103	3.943
5	0.290	2.64×10^{-5}	2.64×10^{-5}	-0.607	1262.00	-8.380	4.697
10	0.372	3.38×10^{-5}	3.38×10^{-5}	-0.629	387.80	-8.533	3.795
15	0.398	3.61×10^{-5}	3.61×10^{-5}	-0.598	1612.00	-8.743	6.855
20	0.434	3.94×10^{-5}	3.94×10^{-5}	-0.605	651.50	-10.030	5.104

Open circuit potential (OCP) analysis

The OCP plots indicating the active-passive transition behavior and thermodynamic characteristics of aluminium matrix composites at 0%, 5% and 20% BT and CN particulate concentration from 3.5% NaCl and 0.05 M H₂SO₄ solution are shown from Fig. 3a to 4b. Figure 3a shows the OCP plots with respect to BT and CN particulate concentration from 3.5% NaCl concentration. The corresponding close-up view of Fig. 3a is shown in Fig. 3b. Figure 4a shows the OCP plots with respect to BT and CN particulate concentration from 0.05 M H₂SO₄ solution while Fig. 4b shows the corresponding close-up view of Fig. 4a. Observation of Fig. 3a shows the OCP plot at 0% BT and CN concentration was scanned at the most electropositive potential values indicating the evolution and growth of protective oxide of the alloy surface. The plot initiated at -1.082 V (0 s) and briefly alternated in potential till 102.3 s at -1.091 V. Beyond this point a sharply increase in potential occurred till -0.675 V at 712 s. The sharp increase is related to oxide formation as earlier explained. The plot configuration from 712 s shows active-passive transition behavior associated with the breakdown and reformation of the protective oxide which is thermodynamically unstable. The plot at 5% and 20% CS particulate concentration exhibited thermodynamic stability from 700.01 s and 712.01 s at -0.850 V and -0.675 V till -0.825 V and -0.770 V at 5400s. Potential transients are relatively minimal due to stability of the surface properties of the composite in the presence of CN particulates. Comparing this to the plot configuration for the composite at 5% and 20% BT concentration, it is clearly visible that the plots with BT reinforced aluminium matrix composite is thermodynamically relatively unstable. Both plots shifted in the positive direction from electronegative values of -1.063 V and -0.994 V at 0 s. Relative stability was attained at -0.858 V and -0.836 V at 602.3 s and 900.01 s. However, the plot configuration showed significant active passive transition behavior and thermodynamic instability relative to the plots for CN particulate reinforced aluminium matrix composite.

The plot configuration in Fig. 4a are generally similar. The plots are produced due to the surface interaction of the matrix composites with SO₄²⁻ anions. The debilitating and high reactivity of the anions results in increase in general corrosion rates compared to the values from NaCl solution. The plots generally shifted from potential values of -0.586 V, -0.726 V, -0.865 V, -0.533 V and -0.480 V for the composite at 0% BT and CN particulate concentration, the composites at 5% BT and CN concentration, and the composites at 20% BT and CN concentration. The potential shift is significantly electropositive for the first 80 s due to instantaneous oxide formation in the presence of adsorbed O₂. However, collapse of the oxide occurred till about 330 s due to the oxidation reaction effect of the SO₄²⁻ anions within the electrolyte. However, competitive adsorption between the dissolved O₂ and SO₄²⁻ anions ensures the gradual formation of the protective oxide on the composite surfaces till 5400 s. The lack of active-passive transition behavior shows the protective oxide formed is thermodynamically stable. This is explained on the basis that Cl⁻ anions are relatively small compared to SO₄²⁻ anions are responsible for localized corrosion such as pitting, whereas SO₄²⁻ anions are usually responsible for general corrosion. Thus, it is probable that the oxide formed on the composite surface in the presence of SO₄²⁻ anions is much thinner than the oxide in the presence of Cl⁻. It must also be noted that the composite at 0% BT and

CN particulate concentration exhibited thermodynamic instability from 2900.82 s (-0.540 V) till 5400 s (-0.517 V). Whereas in the presence of both composites, thermodynamic instability was absent.

Passivation and pitting corrosion evaluation

Potentiostatic data for BT and CN particle reinforced aluminium matrix composites are shown in Table 5. The passivation potential represents the potential at which adsorbed O_2 atoms react with the valence Al electrons on the composite surface resulting in the formation of the protective responsible for the corrosion resistance of the composite. This reaction mechanism occurs following anodic polarization of the matrix composites with respect to particulate concentration. The pitting potential represents the potential at which collapse of the protective oxide occurs, and pit formation, growth and propagation occurs. The passivation range depicts the resilience of the protective oxide before its collapse due to pit formation and growth. The passivation range values for the BT and CN particle reinforced composites in the chloride solution are significantly greater than the corresponding values in the sulphate solution. The passivation range values ranged from - 0.37 V to -0.28 V for BT reinforced composites while the corresponding values for CN reinforced composite ranged from - 0.37 V to -0.34 V. This confirmation aligns with the higher corrosion rate values obtained by the composites in the sulphate solution, signifying significant weakening of the protective oxide by the debilitating action of SO_4^{2-} anions. The values for BT reinforced composites in the sulphate solution ranged from - 0.15 V to -0.14 V, while the corresponding values for the CN reinforced composite ranged from - 0.15 V to -0.11 V. BT and CN particle reinforced aluminium matrix composites exhibits higher resistance to localized corrosion in the chloride solution. Passivation of BT and CN particle reinforced composites in the chloride solution occurred at more electronegative potentials compared to the corresponding values in the sulphate solution with respect to the corrosion potential of the polarization plots.

Table 5
Potentiostatic data for BT and CN particle reinforced aluminium matrix composites in 3.5% NaCl and 0.05 M H₂SO₄ solution

3.5% NaCl Solution				0.05 M H ₂ SO ₄ Solution		
BT Reinforced Matrix Composite	Passivation Potential	Pitting Potential	Passivation Range	Passivation Potential	Pitting Potential	Passivation Range
AB	-1.04	-0.67	-0.37	-0.55	-0.40	-0.15
A2	-1.05	-0.66	-0.39	-0.57	-0.43	-0.13
A3	-0.92	-0.67	-0.25	-0.56	-0.40	-0.16
A4	-0.95	-0.67	-0.28	-0.54	-0.36	-0.18
A5	-0.95	-0.67	-0.28	-0.52	-0.39	-0.14
CN Reinforced Matrix Composite	Passivation Potential	Pitting Potential	Passivation Range	Passivation Potential	Pitting Potential	Passivation Range
AB	-1.04	-0.67	-0.37	-0.55	-0.40	-0.15
B2	-0.91	-0.68	-0.23	-0.56	-0.43	-0.13
B3	-0.86	-0.69	-0.17	-0.58	-0.34	-0.24
B4	-0.93	-0.67	-0.26	-0.55	-0.47	-0.08
B5	-1.02	-0.68	-0.34	-0.56	-0.45	-0.11

Optical and scanning electron microscopy analysis

The optical representative images of aluminium alloy and the aluminium matrix composites are shown from Fig. 5a to Fig. 8b. Figure 5a and b depict the representative images of aluminium alloy and BT/CN particle reinforced aluminium matrix composite before corrosion at mag. x40 and x100. Figure 6a and b depict the optical representative images of aluminium alloy after corrosion in 3.5% NaCl solution and 0.05 M H₂SO₄ solution at mag. x10, x40 and x100. Figure 7a and b depict the optical representative images of BT and CN (20% concentration) particle reinforced aluminium matrix composites from 3.5% NaCl solution at mag. x10, x40 and x100. Figure 8a and b depict the optical representative images of BT and CN (20% concentration) particle reinforced aluminium matrix composites from 0.05 M H₂SO₄ solution at mag. x10, x40 and x100. The optical images in Fig. 6a and b significantly differ from each other due to differences in the reaction mechanisms of the corrosive species. Figure 6a shows corrosion along the grain boundary in line with the established understanding of Cl⁻ anions as being primarily responsible localized corrosion at vulnerable points and regions on metallic alloys especially after

penetration of the protective oxide at weak areas. Limited corrosion occurred outside the grain boundaries, whereas Fig. 6b shows general surface deterioration at specific areas of the alloy surface by SO_4^{2-} anionic species. The degree of deterioration is much more extensive compared to Fig. 6a. The purpose of Fig. 6a and b is to compare the effect of reacting anions with and without the presence of BT and CN particle reinforcements. The images in Fig. 7a and b which depicts the effect of Cl^- anions on the corrosion resistance of BT and CN particle reinforced aluminium matrix composites shows that CN reinforced composite (Fig. 7b) is more resilient to Cl^- anionic attack due to the absence of localized and general corrosion compared to BT reinforced composite (Fig. 7a) where the extent of localized deterioration partially increased though superficial with respect to corrosion rate results. General corrosion also appeared visible but magnifications at x100 shows the deterioration is also superficial. However, in the presence of SO_4^{2-} anions (Fig. 8a and b) morphological deterioration is limited and superficial compared to Fig. 6b. The presence of BT and CN particle reinforced composites enhanced the resistance of the reinforced composites to corrosion.

The SEM images for the aluminium alloy, and BT and CN reinforced aluminium matrix composites are shown from Fig. 9a to Fig. 11b. Figure 9a and b depict the representative SEM image of aluminium alloy at 0% particulate concentration before and after corrosion. Figure 10a and b depict the representative images of BT and CN particle reinforced aluminium composite at 20% concentration before corrosion. Figure 11a and b depict the representative images of BT and CN particle reinforced aluminium composite at 20% concentration after corrosion. Significant variation of aluminium alloy morphology is visible for Fig. 9a and b. Figure 9b shows a severely degraded morphology with significant corrosion pits. Corrosion along the grain boundaries are also visible. These observations occurred due to oxidation and subsequent degradation of the surface properties of the aluminium alloy. The presence of BT and CN particulate reinforcements within the aluminium matrix composites influenced the surface properties and morphology of the composites before corrosion as shown in Fig. 10a and b. Corrosion resistance of BT and CN particle reinforced composites significantly varies as shown in Fig. 11a and b. Figure 11a shows significant wear of BT reinforced composite morphology, extensive intergranular corrosion and limited pit degradation. However, Fig. 11b shows extensive general corrosion, intergranular corrosion and extensive corrosion pits.

X-Ray Diffractometry

Figure 12a and 12b presents the diffraction graph for aluminium alloy prior to and subsequently after corrosion while Fig. 13a and 13b presents the diffraction graphs for BT reinforced aluminium matrix prior to and subsequently after corrosion. Figure 14a and 14b presents the diffraction graphs for CN reinforced aluminium matrix prior to and subsequently after corrosion. The peaks of the diffraction graphs for sample AB before and after corrosion are shown in Fig. 12a and Fig. 12b at specific 2θ values. The dominant diffraction peaks in Fig. 12a are Al_2O_3 , Fe_2O_3 , ZnS and CuS_2 . Al_2O_3 evolves and grows on the aluminium alloy, passivating its surface and providing significant corrosion protection. Fe_2O_3 is a corrosion product of Fe oxide due to the reaction of Fe with O_2 and moisture. As a result of its active

nature corrosion reaction on the Fe impurity is progressive [36]. CuS_2 is a secondary corrosion product, primarily resulting from corrosion of Cu corrosion in corrosive environments [37–39]. ZnS_2 , ZnCO_3 and CuO_2 are insoluble corrosion products which contributes to the corrosion resistance of the alloy [40–42]. After corrosion, as shown in Fig. 12b, the dominant phases are generally the same. However, variation of peak value shows significant alteration of the crystallographic properties of the alloy while the phases compounds are generally the same. The electrochemical properties of the alloy remain unchanged due to repassivation of the dominant Al_2O_3 protective oxide film.

Observation of Fig. 13a shows the dominant phase compounds formed (Al_2O_3 , CuS_2 , ZnS_2 , ZnCO_3 and CuO_2) occurred at specific 2θ values. Comparing these to Fig. 14a the dominant phases (Al_2O_3 , Fe_2O_3 , SiO_2 , ZnS_2 , ZnCO_3 , MnO , CaCO_3 and FeS) occurred at specific 2θ values. The presence of protective Al_2O_3 on the peaks of the diffraction graphs for BT particle reinforced matrix composite (Fig. 13a) at different diffraction angles coupled with the corrosion resistance enhancement effect of ZnS_2 , CuO_2 and the newly identified SiO_2 [43–45], shows the phases identified in Fig. 13a enhances the corrosion resistance of BT particle reinforced aluminium matrix composite compared to CN particle reinforced matrix composite. The presence of MnO , FeS and CaCO_3 [46–49], negatively impacts the corrosion resistance of the CN particle reinforced aluminium matrix composite though the positive influence of other phases compounds were acknowledged as earlier discussed. Most of the graphical peaks of the dominant phases in Fig. 13b and 14b significantly varied in 2θ value, crystallographic orientation and has decreased. Polarization results shows BT particle reinforcement generally decreased the corrosion rate of the reinforced aluminium alloy compared CN reinforced matrix composite whose influence is subjective with respect to concentration and corrosive solution. Hence, the identified phases show the corrosive anions has limited influence on the corrosive resistance of the particle reinforced composites as the electrochemical properties of the phases present counteracts and compliments each other.

Conclusion

Bos taurus (BT) particle reinforced aluminium matrix composite exhibited moderately higher corrosion resistance than *Cocos nucifera* (CN) particle reinforced aluminium matrix composite. Corrosion resistance of BT reinforced composite increased with increase in BT wt. concentration compared to CN reinforced matrix composite where corrosion rate was determined to progressively increase. Both BT and CN particle reinforced composite displayed significant passivation characteristics at low particle wt. concentration due to limited galvanic action between the particulates and the substrate aluminium alloy. They displayed significant resistance to localized corrosion compared to the monolithic aluminium alloy. However, open circuit potential analysis shows significant active-passive transition behavior and thermodynamic characteristics of the heterogeneous microstructural properties of the aluminium composites. Severely degraded morphology, corrosion pits, and intergranular corrosion visible on the monolithic aluminium alloy were absent on the particle reinforced aluminium matrix composite. The presence of the particulate reinforcements enhanced the localized corrosion resistance of the aluminium composites.

Declarations

- Competing interest statement

Author declares no conflict of interest exists

- Author contributions

Roland Tolulope Loto is responsible for Supervision, Conceptualization and Writing- Original draft preparation. Ademola Ogunleye, Adeniyi Oladipupo, Sonia Ofordum and Abisola Ale are responsible for Visualization, Investigation, Validation, Methodology, Data curation and Writing- Original draft preparation

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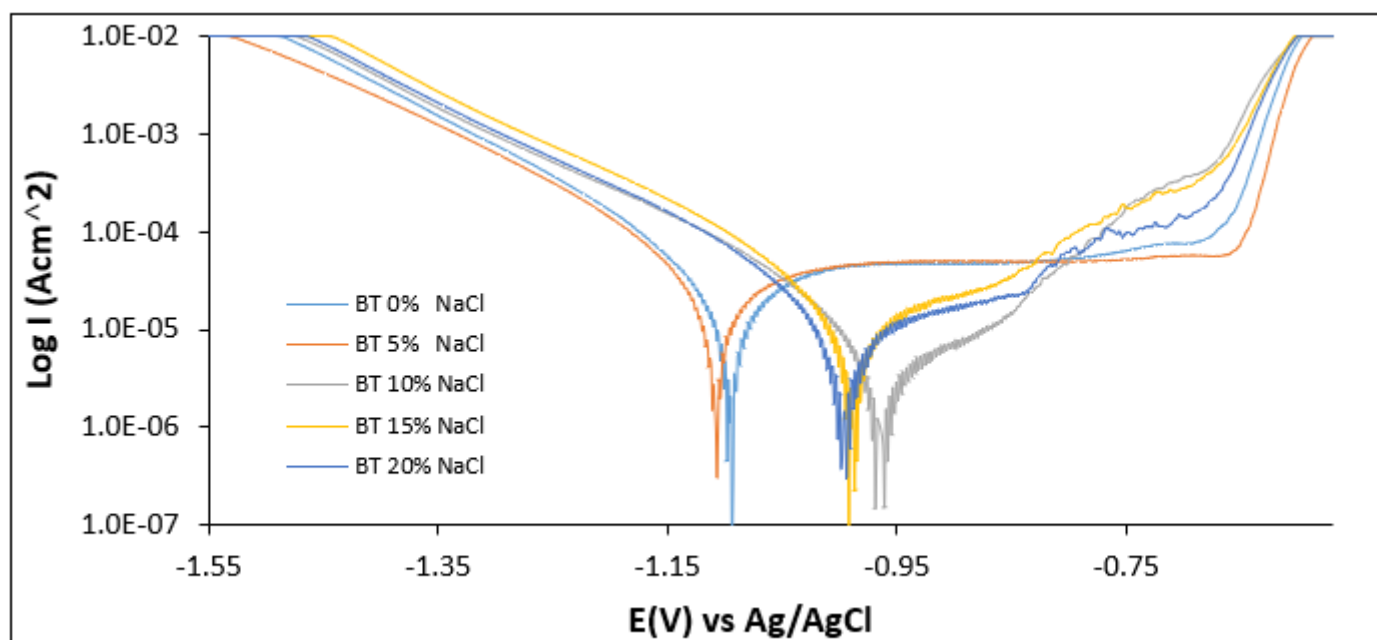
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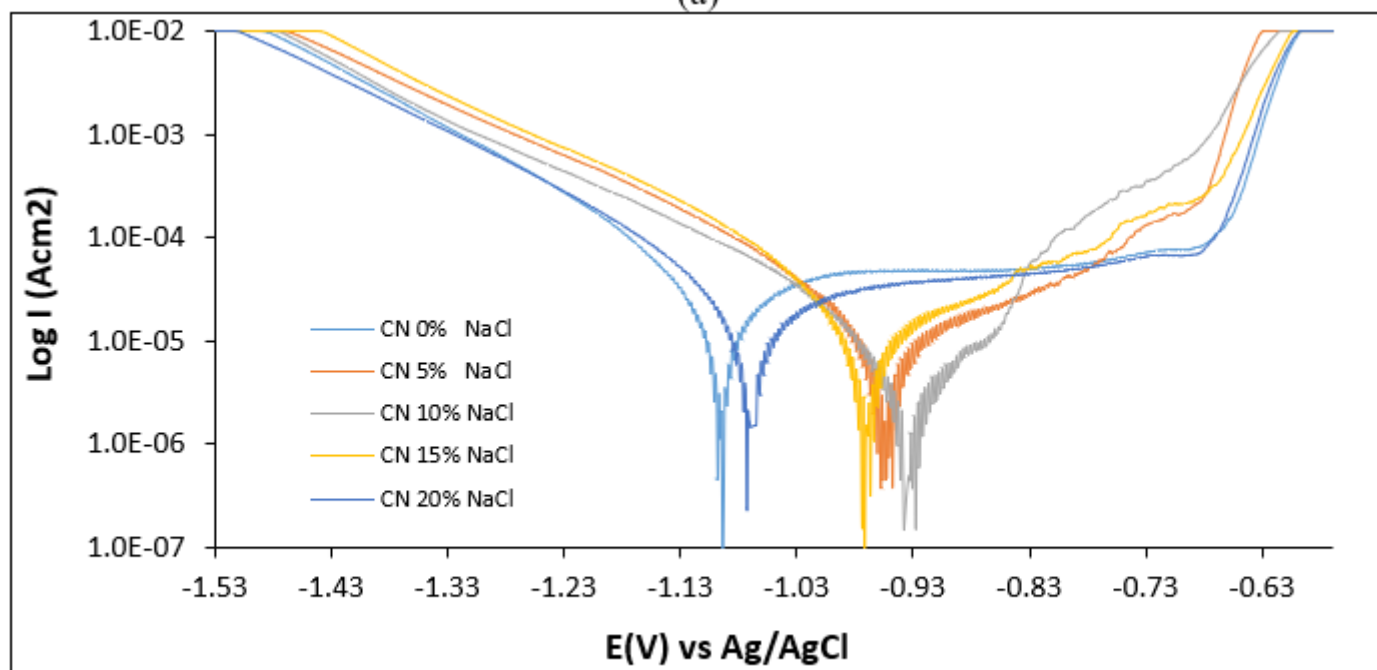
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Figures



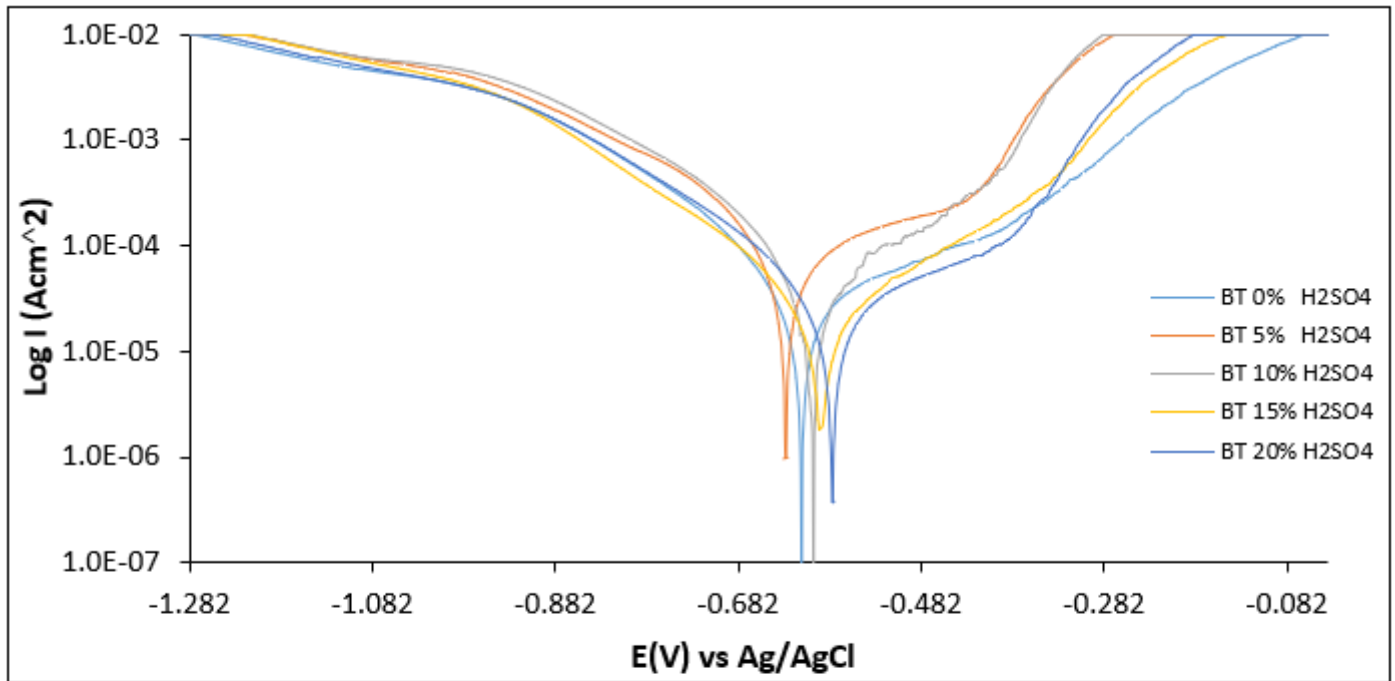
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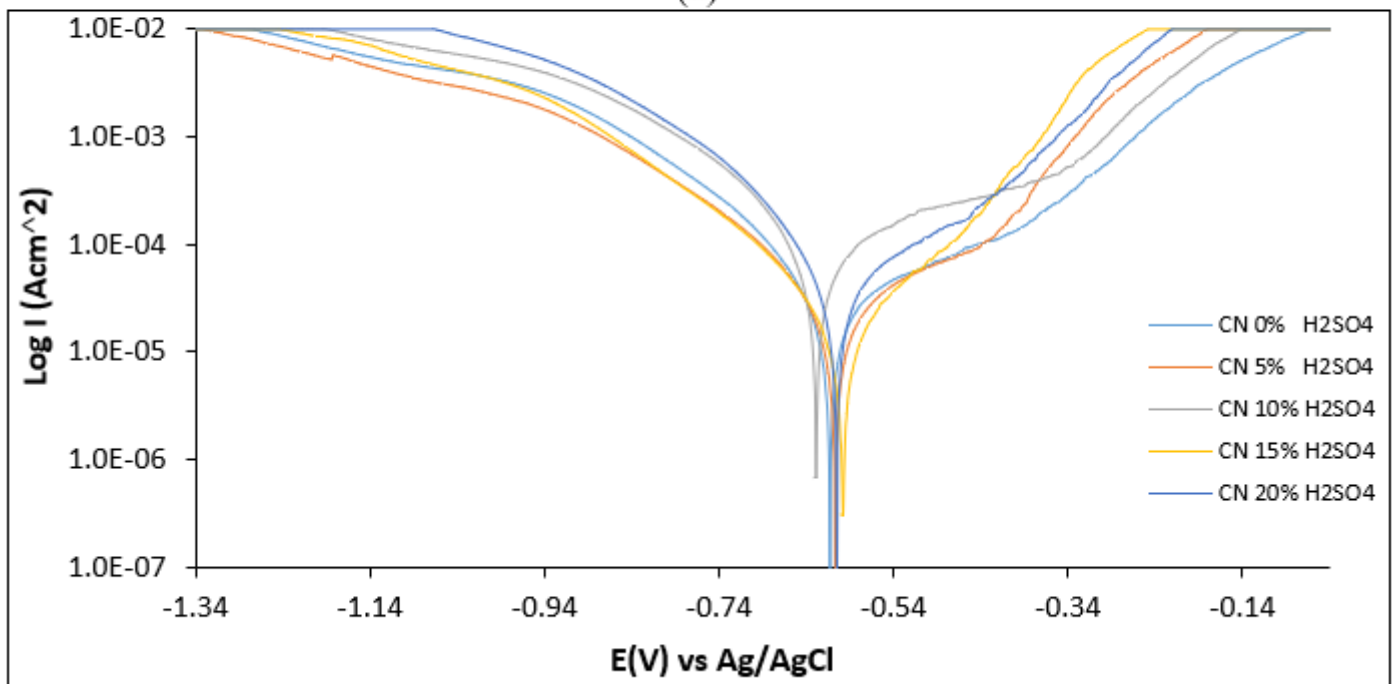
(b)

Figure 1

Potentiodynamic polarization plots for (a) BT and (b) CN aluminium matrix composites from 3.5% NaCl solution



(a)



(b)

Figure 2

Potentiodynamic polarization plots for (a) BT and (b) CN aluminium matrix composites from 0.05 M H_2SO_4 solution

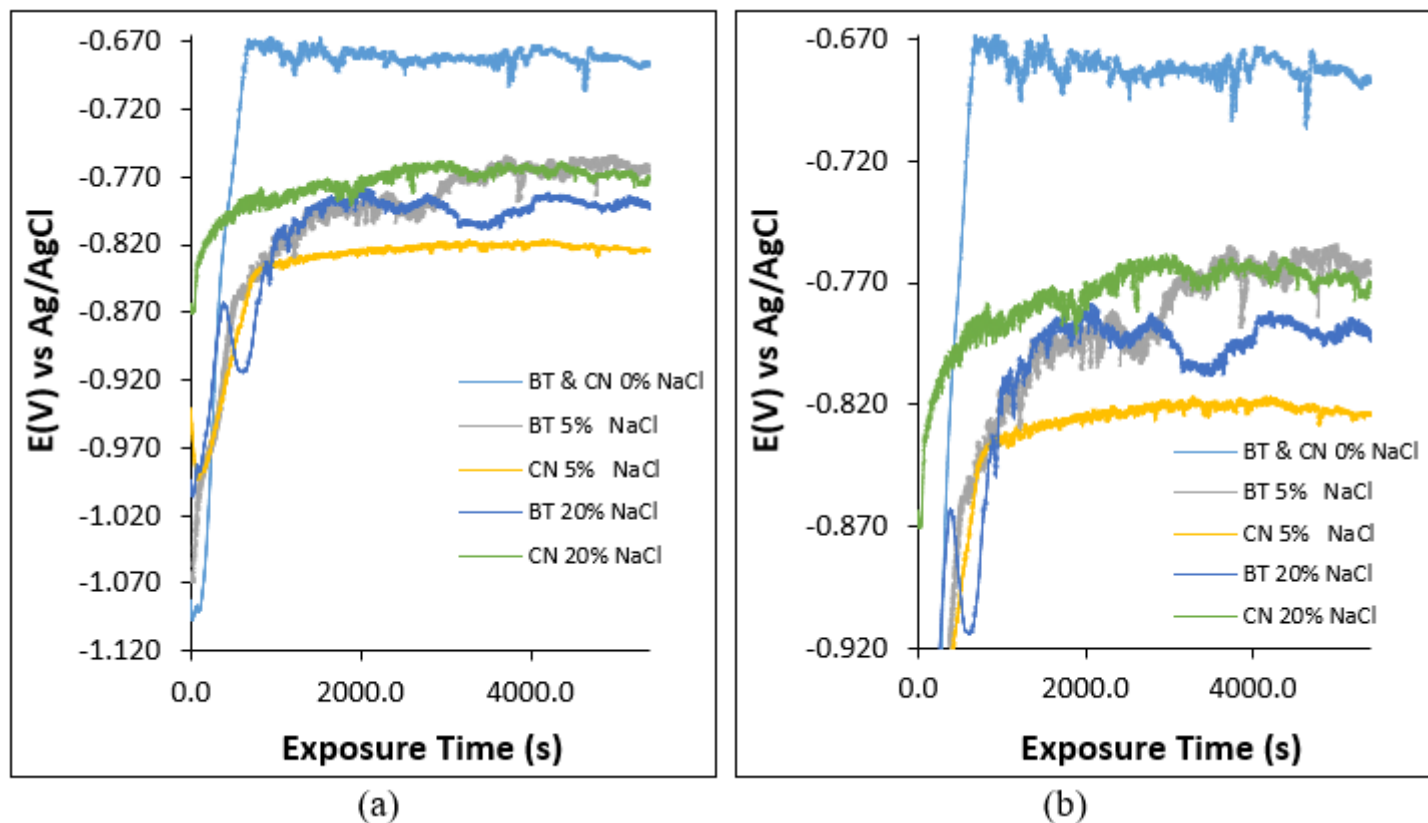


Figure 3

OCP plots of (a) BT and (b) CN particulate reinforced aluminium matrix composites at 0%, 5% and 20% concentration from 3.5% NaCl concentration

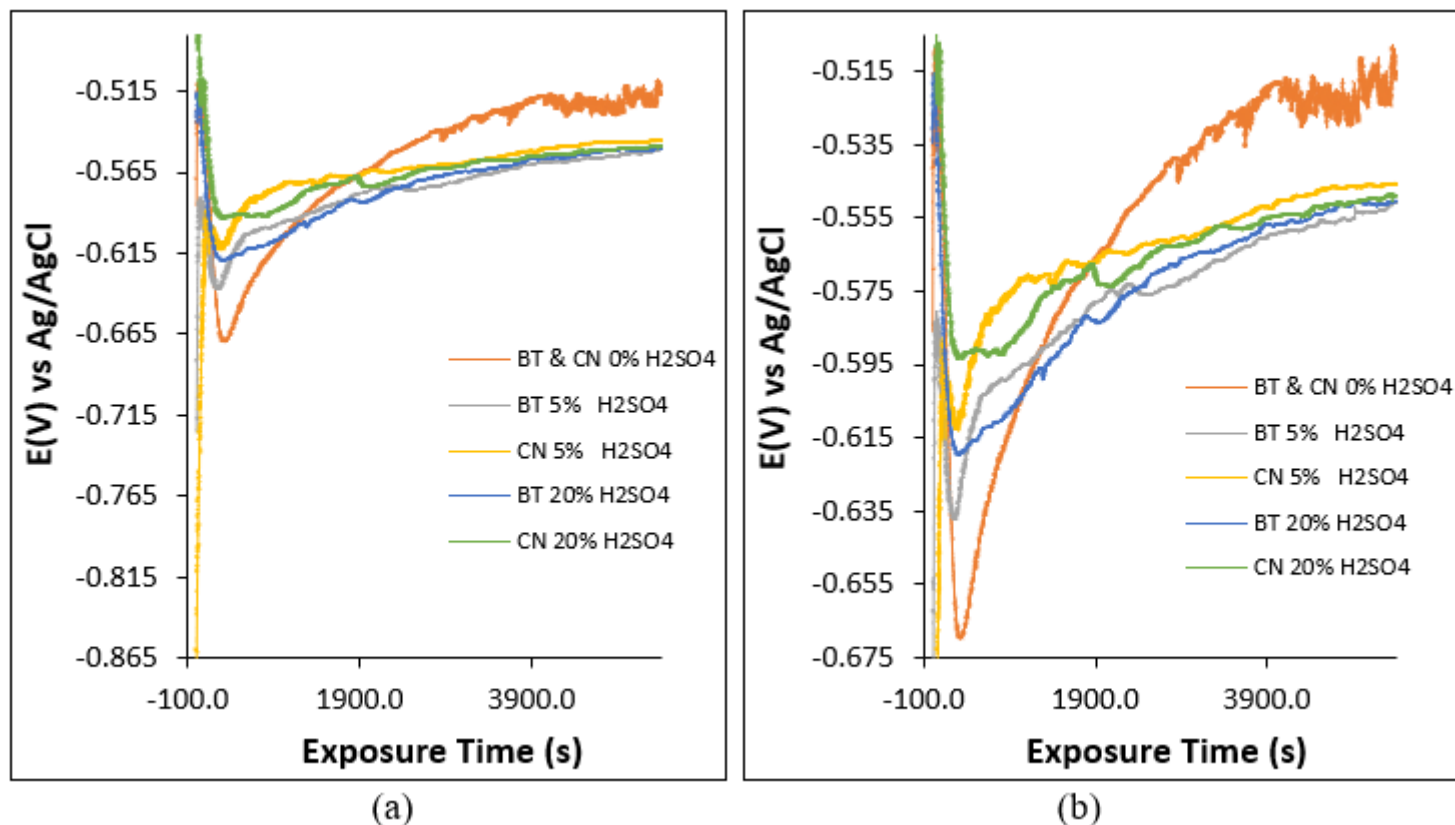


Figure 4

OCP plots of (a) BT and (b) CN particulate reinforced aluminium matrix composites at 0%, 5% and 20% concentration from 0.05 M H_2SO_4 concentration

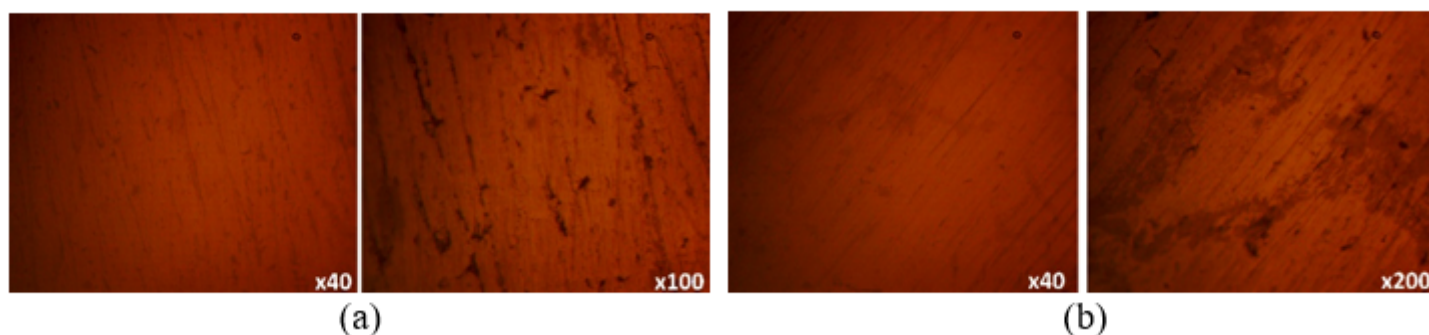


Figure 5

Optical representative images of (a) aluminium alloy and (b) BT/CN particle reinforced aluminium matrix composite before corrosion at mag. x40 and x100

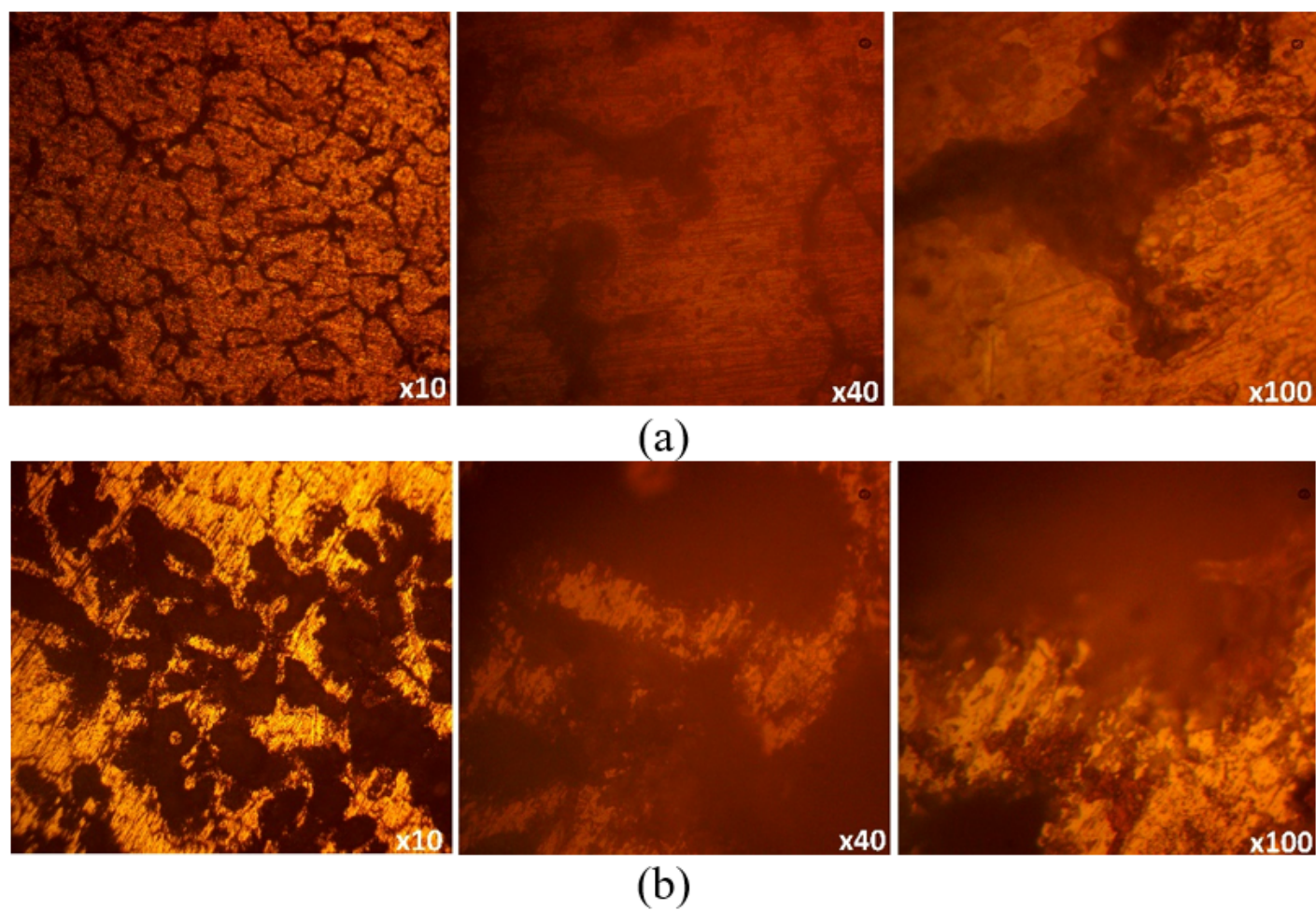


Figure 6

Optical representative images of aluminium alloy after corrosion in (a) 3.5% NaCl solution and (b) 0.05 M H₂SO₄ solution at mag. x10, x40 and x100

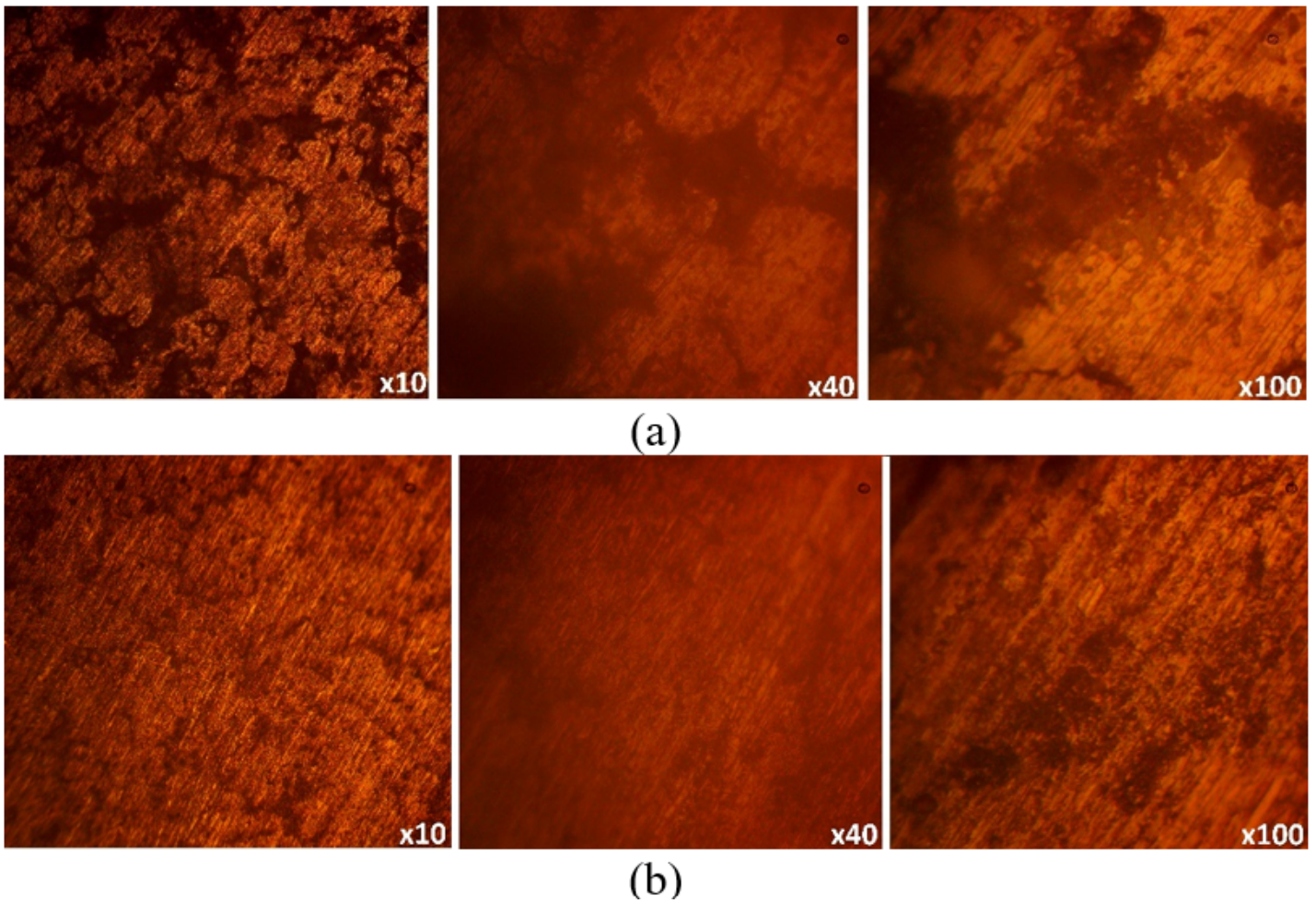


Figure 7

Optical representative images of (a) BT and (b) CN (20% concentration) particle reinforced aluminium matrix composites from 3.5% NaCl solution at mag. x10, x40 and x100

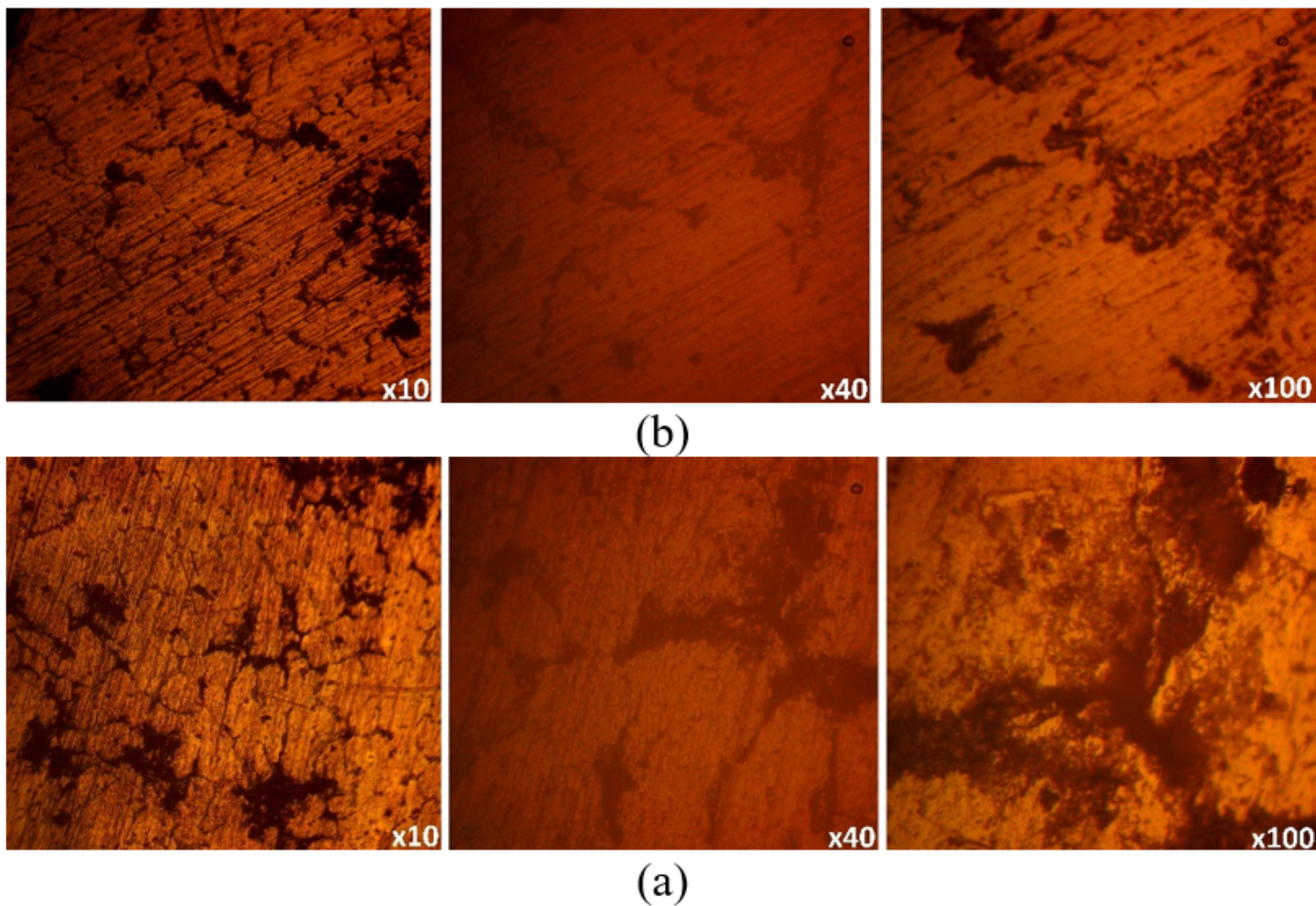


Figure 8

Optical representative images of (a) BT and (a) CN (20% concentration) particle reinforced aluminium matrix composites from 0.05 M H_2SO_4 solution at mag. x10, x40 and x100

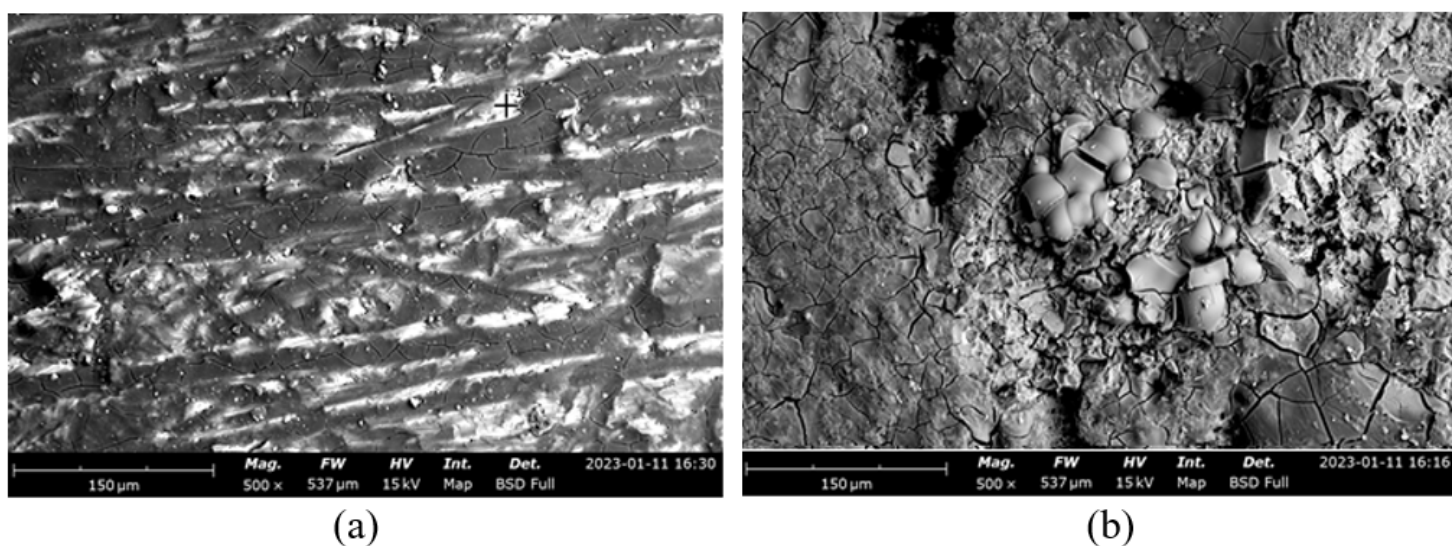


Figure 9

SEM representative images aluminium alloy at 0% BT and CN particle concentration (a) before corrosion and (b) after corrosion

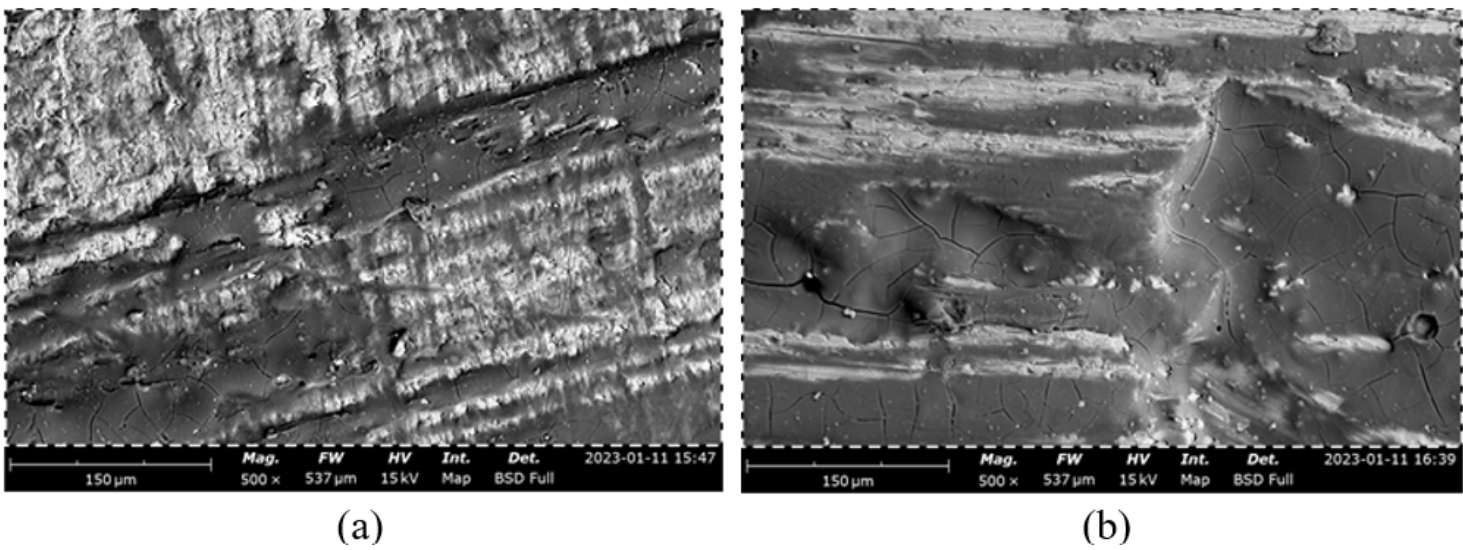


Figure 10

SEM representative images aluminium matrix composite at (a) 20% BT and (b) 20% CN particle concentration before corrosion

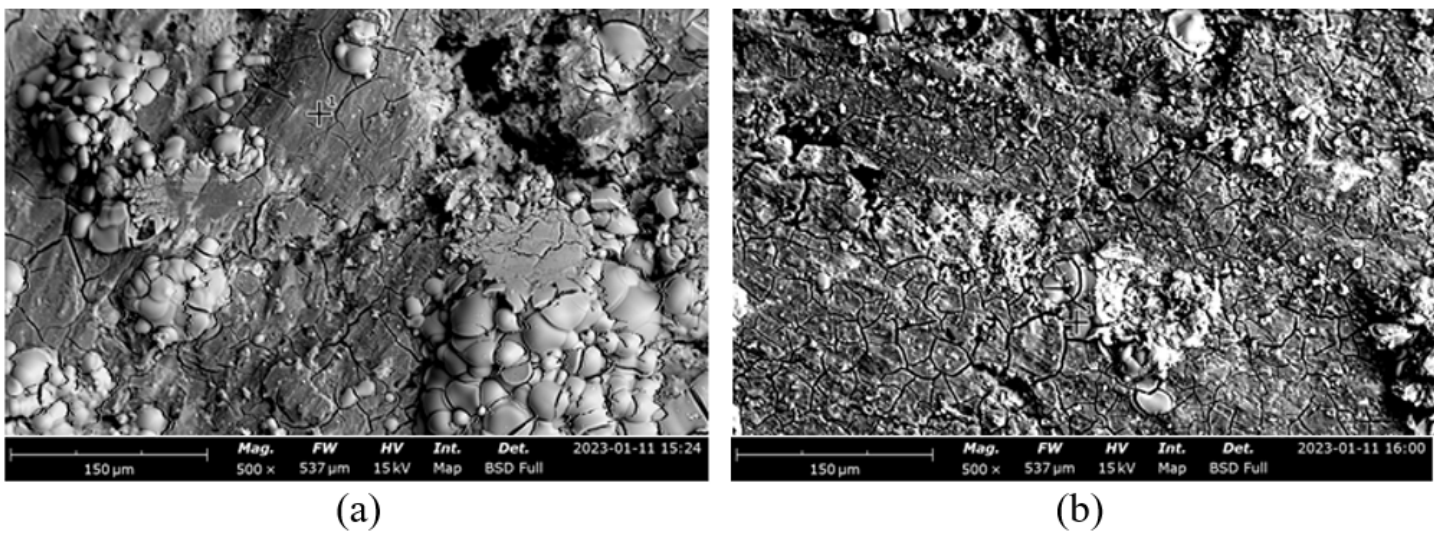
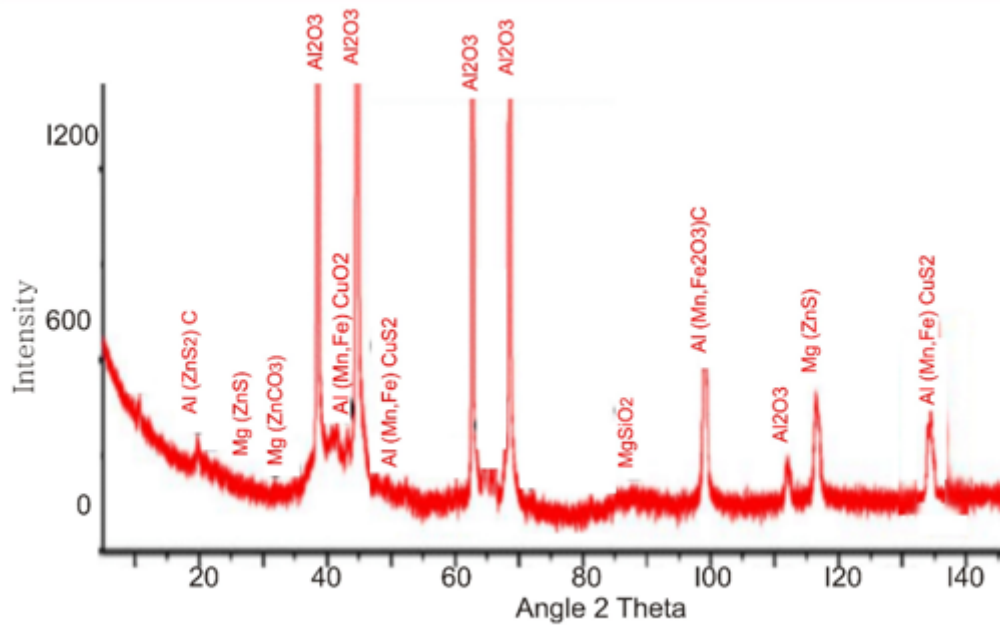
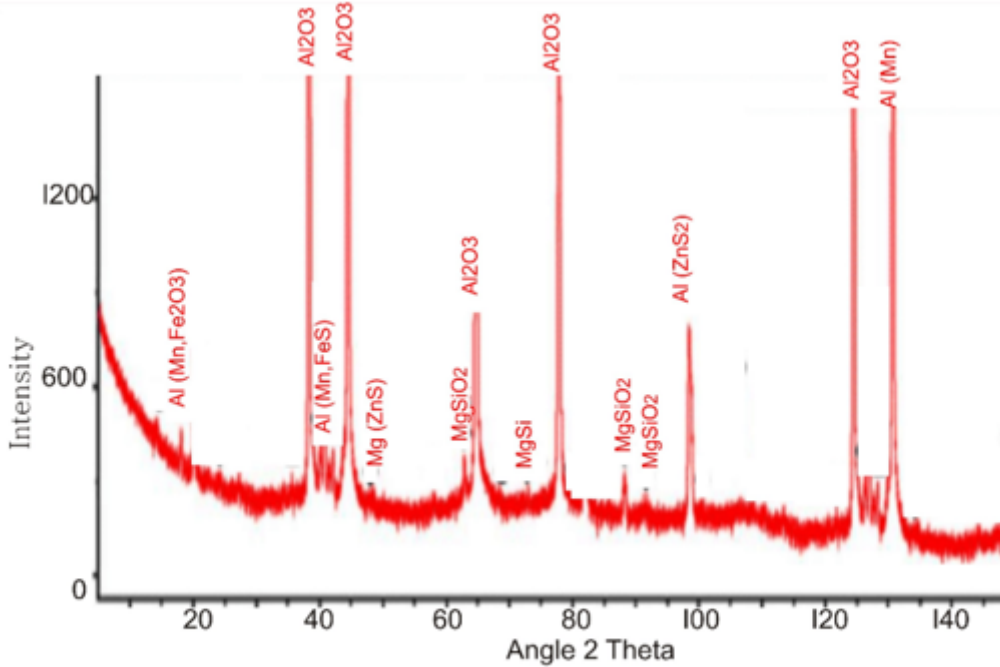


Figure 11

SEM representative images aluminium matrix composite at (a) 20% BT and (b) 20% CN particle concentration after corrosion



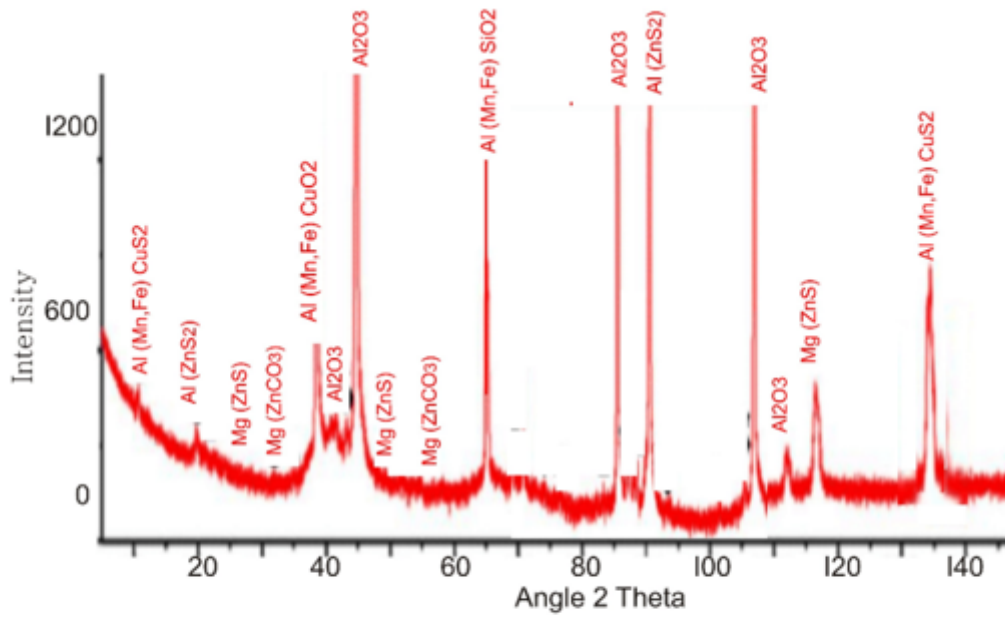
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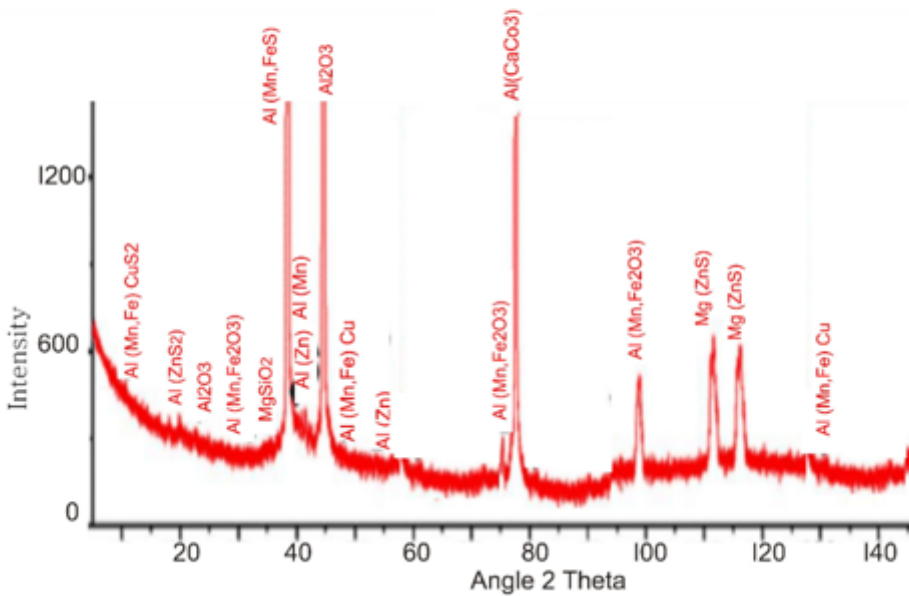
(b)

Figure 12

Representative XRD Phase identification graph for aluminium alloy (a) prior to corrosion test and (b) after corrosion test



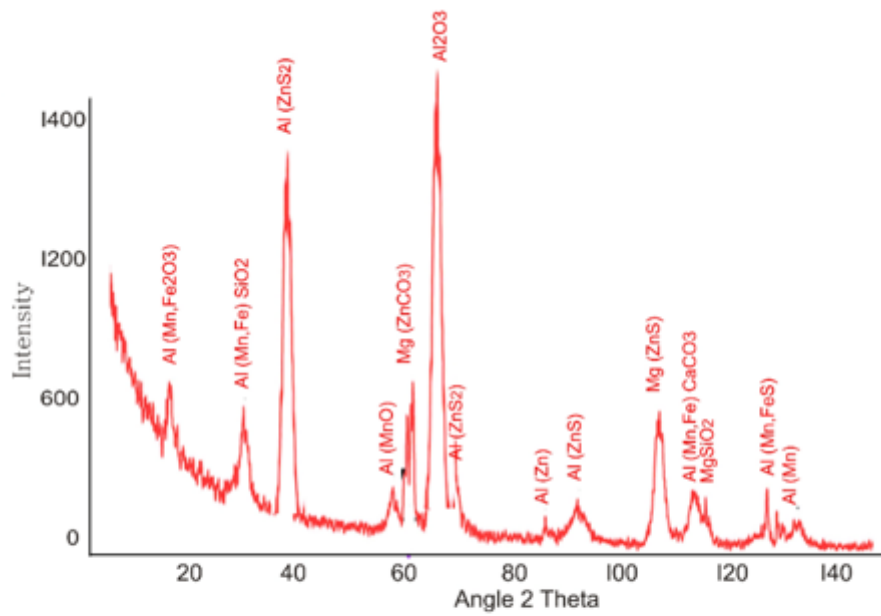
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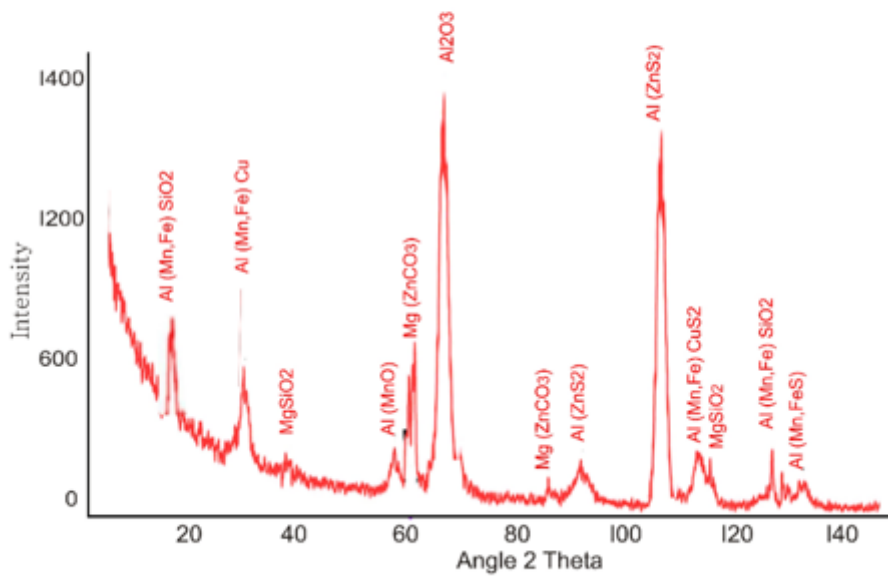
(b)

Figure 13

Representative XRD Phase identification graph for BT particle reinforced aluminium matrix composite (a) prior to corrosion test and (b) following corrosion test



(a)



(b)

Figure 14

Representative XRD Phase identification graph for CN particle reinforced aluminium matrix composite (a) prior to corrosion test and (b) following corrosion test