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Electrical and Corrosion Behaviour of Aluminium-Aluminium Nitride Particulate Composite produced via Powder Metallurgy

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Research Article

Abstract

The properties of aluminium nitride (AlN) such as good coefficient of thermal expansion, good wear and corrosion resistance, high mechanical strength, good resistance to thermal shock and good electrical properties have continued to attract research attention in recent times. In this paper, the interest is to investigate the influence of AlN on the electrical conductivity and corrosion properties of Al-AlN particulate composite produced using powder metallurgy. The samples were compacted using the pressure of 450MPa and sintered at 550 °C for 30 minutes using the two-step sintering method. Four-point probes machine was used to determine the electrical resistivity and subsequently the electrical conductivity of the samples. The samples were immersed in 0.05M NaOH for 24 hours to determine their corrosion behaviour using the weight loss method. The corroded samples were characterized using X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). The result of the electrical conductivity of the samples increased with both the amount of reinforcement and magnesium added. The unreinforced aluminium sample recorded the lowest value of electrical conductivity while the sample with composition Al-16.25wt%AlN-1.0wt%Mg gave the highest value, 131.33 $(\Omega m)^{-1}$. The results of XRD analyses revealed peaks of aluminium hydroxide ($Al(OH)_3$) as the main corrosion product on the samples. The results show that corrosion rates of the samples decrease with weight fractions of AlN and Mg. The sample containing Al-16.25wt%AlN-1.0wt%Mg offered the best corrosion resistance with a corrosion rate equivalent to 22.74mm/y; while the unreinforced aluminium sample corroded the most, 37.19mm/y.

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Keywords
Composite, Corrosion, electrical conductivity, Powder Metallurgy, XRD

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1. Introduction

Aluminium nitride (AlN),a non-oxide ceramic, is characterized by the following properties: high melting point about 2800°C, low coefficient of thermal expansion, high mechanical strength, good wear and corrosion resistance and good resistance to thermal shock (Du *et al*., 2023; Kim *et a*l., 2022; Kim *et al*., 2015; Polycarp, *et al*., 2015; *Qadri, et al., 2017)*;and it is also has these electrical properties: dielectric strength 15 V/m, and dielectric constant 8.9 (1MHz) (Nasery, *et al*., 2011). These properties of AlN make it a good candidate for use in the electronic industry (Bian *et al*., 2015). It is employed in heat sinks for mainframes in supercomputers, electro-optics, as potential replacements for alumina and field emission devices, light-emitting diodes, fiber or filler to improve the thermal properties for electronic packaging, and for enhancement of thermal properties of glasses or polymers (Angappana, *et al*., 2013; Suehiro, *et al*., 2002a). These qualities have made AlN a suitable candidate in different areas of applications in the 21st century due to the advancement in technology and the need to produce advanced materials to meet the present demands. Composite materials, whose properties could be tailored to meet any given requirements, play major roles in advanced materials (Cantor, *et al.*, 2003). However, the Sintering of powder compacts helps in boding the reinforcement to the matrix through the application of heat to bring out the desired properties (Baba, 2016; German, 1996); but this process cannot be achieved when the matrix fails to wet the reinforcement. Wetting liquids usually have small contact angles and are capable of spreading over the solid particles; hence facilitating the bonding process during sintering (German, *et al*., 2009). Magnesium powder is usually added to enhance the wetting process during the sintering of aluminium matrix composite (Schaffer and Hall, 2002).

Imperfections in materials, such as vacancies, voids, impurity atoms, and the existence of dislocations are the key variables influencing the electrical conductivity of metals. Others such as temperature, alloying elements, and previous processing the material has undergone, such as heat treatment and mechanical shaping, are additional factors that influence the electrical conductivity of materials (Slade, 2013). When it comes to the corrosion resistance of materials, powder metallurgy parts are highly disadvantaged due to their porous nature.

In this paper, the effects of the corrosion-resistant AlN reinforcement on the electrical conductivity and corrosion properties of the Al-AlN composite have been investigated.

2. Materials and Methods

The materials used in this work include; magnesium powder, aluminium, and aluminium nitride powders obtained from Bumi Padu Solution Sdn Bhd, Kuala Lumpur, Malaysia; and Oxygen-free nitrogen (OFN).

The apparatus/equipment used includes digital vernier callipers, stainless steel mold, digital weighing balance, beakers, measuring cylinders, compaction machine, steel tube furnace, four-point probe machine, etc.

2.1 Production of Al-AlN Composite

The as-received Al and AlN were first characterized using the XRD machine to ascertain the initial condition of the raw materials.

The aluminium powder was mixed withreinforcement consisting0, 6.50, 9.75, 13.0, and 16.26wt% AlN to form the composite of different compositions with each mixturetotaling 1.80g by weight.Each composition was poured into a cylindrical mold ofdiameter 10.2mm and pressed using a compaction pressure of 450mpa to form the green compact.

To evaluate the effect of Mg in the composites, the processes above were repeated with the addition of 0.5, 1.0, and 2.0wt%Mg. The compacts were sintered in a nitrogen atmosphere at 550ºC for 30 minutes using a two-step sintering technique. The detail of the fabrication process of this composite hasalready been published elsewhere (Polycarp, *etal*., 2017).

2.2 Electrical conductivity

The electrical resistivities of the Sintered Al-AlN compacts were measured using a four-point probe (Zainal *et al*., 2015). The sample whose resistivity was to be measured was positioned on the wafer beneath the four-point probes and the apparatus was connected to and controlled by a computer. The contact point of the equipment was positioned such that the four probes make contact with the test specimen. The outcomes of the tests were displayed on the computer screen and were recorded.

Equation (1) was used to calculate the bulk resistivity, while equation (2) was used to calculate the electrical conductivity as the reciprocal of electrical resistivity (Aker and Kaya, 2017). The electrical resistivity, τ (Ωcm) is given by

$$\tau = 4.532 \frac{V}{I} tk \quad - \quad - \quad (1)$$

Where V is voltage, I is the current, t is the sample thickness and k is the correction factor.

The electrical conductivity, $\sigma(\Omega M)^{-1}$ is the inverse of resistivity thus:

$$\sigma = \frac{1}{\tau} \quad - \quad - \quad - \quad (2)$$

2.3 Corrosion

Before their immersion in the corrosive medium, the scales on the samples were removed using emery papers and their initial weights recorded. Using threads, the weighed samples were suspended into the beakers containing 50cm^3 of 0.05 M NaOH solution for 24 hours to evaluate the extent of their interactions with the basic environment. Some of the as-removed samples were dried and used for XRD and SEM analyses, while the other samples were immersed in HF-HNO_3 pickling solution for about 3-5 minutes (Keijzer, 2004)to remove the corrosion products on their surfaces. The corroded surfaces of the samples after pickling were characterized using XRD.The weight losses in the samples were recorded and used for the determination of corrosion rate using equation (3) thus (Fontana and Greene, 1987):

$$CR = 87.6 \frac{W}{DAT} \quad - \quad - \quad - \quad (3)$$

where, W= weight loss in milligram (mg), D = density of specimen (g/cm^3), A = specimen area in cm^2 and T = exposure time in hours.

3.0 Results and Discussions

The results of the various tests conducted in the course of this work have been presented and discussed in this section.

3.1 The XRD results of as-received samples

The XRD results of the as-received aluminium and the AlN powder used in this work are shown in Figures 1 and 2 respectively.

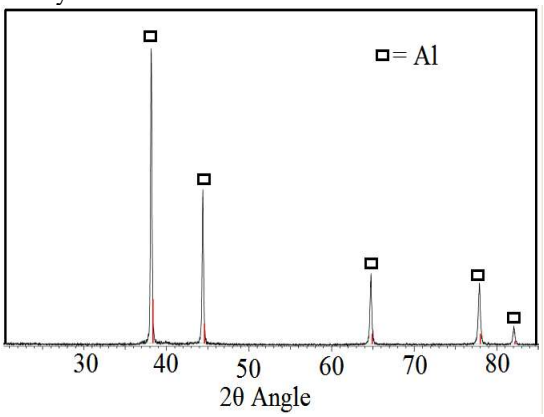


Figure 1. XRD pattern of as-received aluminium powder.

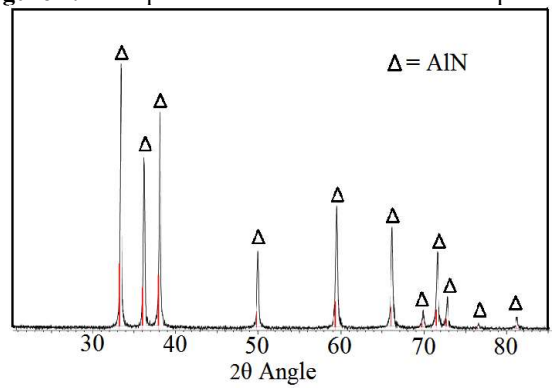


Figure 2. XRD pattern of as-received AlN powder.

The XRD patterns shown in Figures 1 and 2 revealed peaks of Al and AlN respectively. Other peaks observed were

insignificantly low; indicating that the as-received powders had very high percentage purity.

3.2 The Electrical Conductivity Results

The 4-point probe machine measures and plots the graph of current (I) against the voltage (V); the slope of the graph gives the resistivity value for each sample. Figure 3 shows how the amount of reinforcement affects the I-V curves of the composite samples.

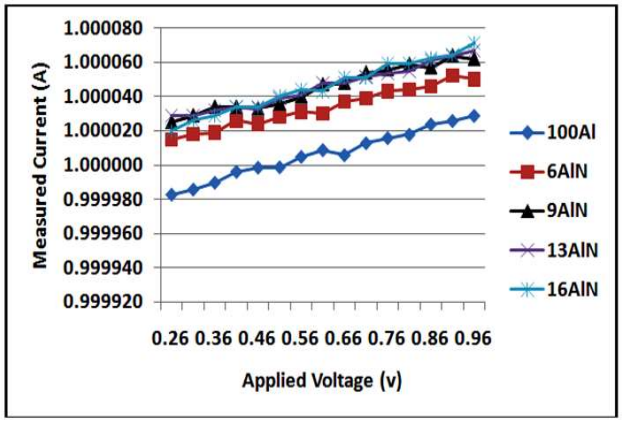


Figure 3. Influence of Reinforcement on I-V the curve

Since the reciprocal of the slope of I-V curve gives the resistivity, it means that the unreinforced aluminium (100%Al) sample whose curve is the lowest in Figure 3 has the highest resistivity values or other words, the lowest values of electrical conductivities; while the composite containing 16wt%AlN gave the highest values of the electrical conductivity.

Knowing that conventional Al has very good electrical conductivity, it will be unimaginable to see unreinforced Al compact having a very low value of electrical conductivity as shown in Figure 3. The reason for this anomaly is that sintered aluminium is usually characterized by Al_2O_3 formed due to oxidation of Al during sintering; the aluminium oxide formed prevents the Al-Al contact which, consequently, reduces the electrical conductivity values (Total-Materia, 2003).

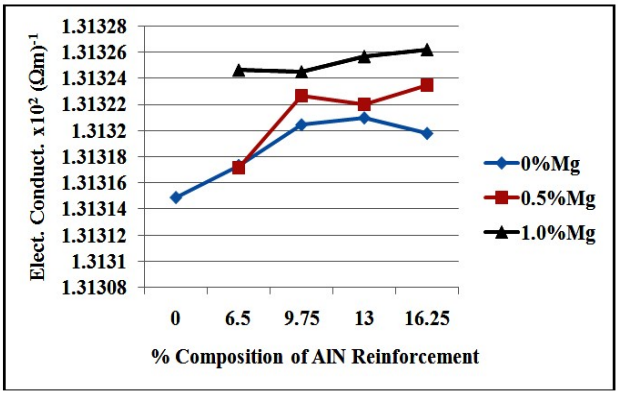


Figure 4. The influence of weight fractions of AlN reinforcement and magnesium on electrical conductivities of the samples.

Figure (4) also shows that the electrical conductivity values of the composites increase with the weight fraction of AlN and the amount of magnesium added. The addition of AlN probably reduces the tendency for the formation of Al_2O_3 hence lowering the resistivity values; while magnesium reduces Al_2O_3 to Al hence promoting Al-Al contact and consequently improving the electrical conductivity values (Mamala and Ścieżor, 2014). However, in aluminium wire, the presence of magnesium will reduce the electrical conductivity values since there is no provision for Al_2O_3 to be reduced hence; magnesium becomes an impurity acting as a barrier to the free flow of electric current (Dybowski, *et al.,* 2016).

3.3 Corrosion Analysis of the Samples

After 24 hours of immersion of the samples in 0.05M NaOH, the XRD results of the corroded samples were analyzed. The XRD patterns in Figure 5 show the corrosion products formed on the unreinforced aluminium sample.

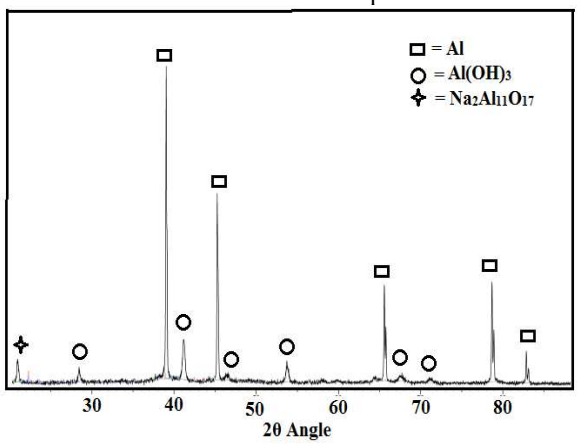


Figure 5. XRD result of 100%Al sample after immersion in NaOH solution for 24 hrs.

The main corrosion products observed were $Al(OH)_3$ (Zhang *et al*., 2009) and $Na_2Al_{11}O_{17}$ while the aluminium peaks maintained their positions at a regular 2θ angle.The XRD results of the other corroded samples have been superimposed in Figure 6 for easy comparison.

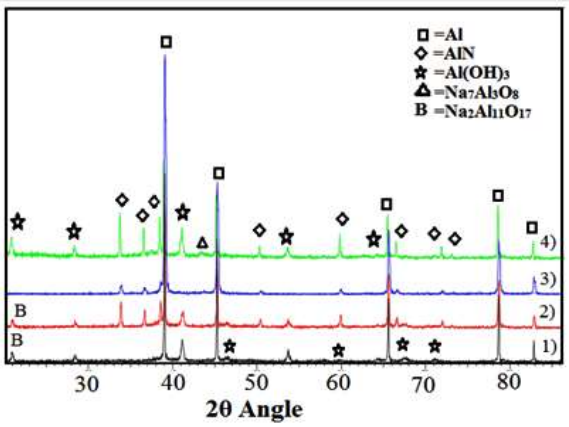


Figure 6:XRD Patterns showing corrosion products on sample: (1) 100%Al, (2)Al-6.5wt%AlN, (3) Al-9.75wt%AlN-

1.0wt%Mg, (4) Al-13.0wt%AlN-2.0wt%Mg after 24hrs immersion in 0.05M NaOH.

Figures 6:(a)-(d) compare the XRD results of three corroded samples to that of the un-reinforced aluminium sample. The corrosion products were all aligned at the same position on the 2θ angle scale except the result of the sample with the compositionAl-13wtAlN-2.0wt%Mg(Figure 6 (d)) where an additional corrosion product; $Na_7Al_3O_8$was observed at 2θ angle of 43°. The reinforced samples also revealed peaks of Al and AlN at their regular 2θ angles as reported by Fale *et al*. (2013).

The XRD result of the corroded sample of Al-13wt%AlN-2.0wt%Mg after pickling is presented in Figure 7.

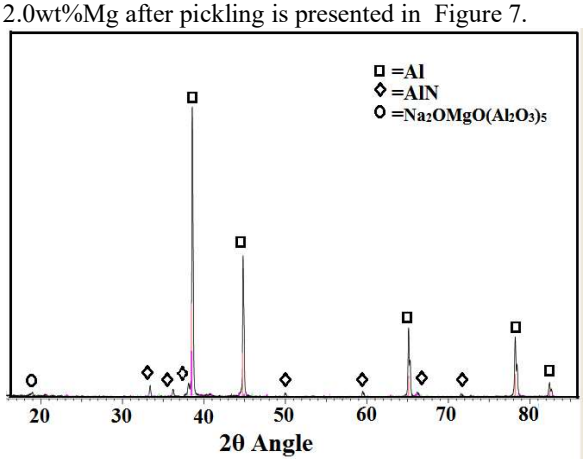
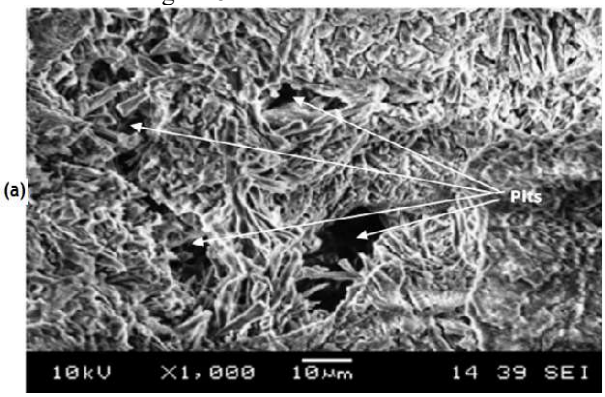


Figure 7: XRD patterns for the sample containing Al-13wt%AlN-2wt%Mg after pickling in a HF-HNO_3 solution.

The XRD patterns in Figure 7 did not reveal any peaks of corrosion products except a new complex compound, $Na_2OMgO.(Al_2O_3)_5$ that was observed at2θangle of 18^0; the same position where the corrosion product; $Na_2Al_{11}O_{17}$.

The emergence of $Na_2OMgO.(Al_2O_3)_5$ on the pickled surface of this sample suggests that it is probably a product of interaction between $Na_2Al_{11}O_{17}$ and the pickling solution (HF-HNO_3) considering that it occupies the same position on the 2θ angle scale. The SEM results of some of the corroded samples are shown in Figure 8.



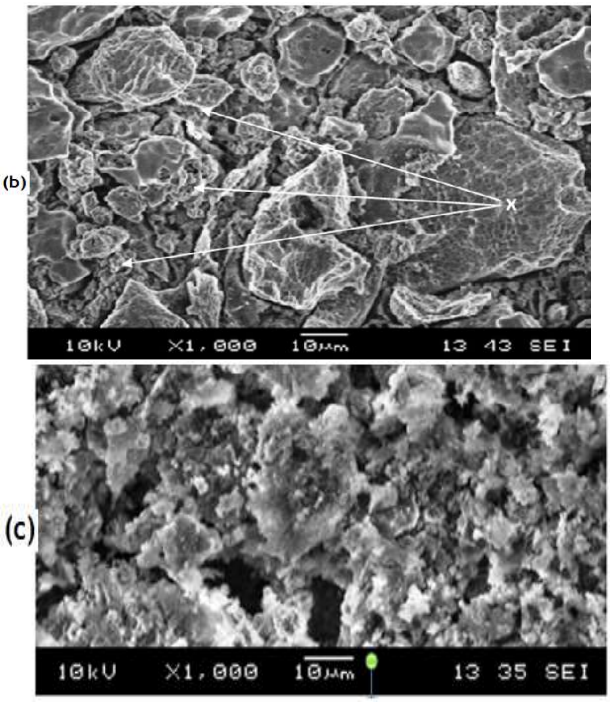


Figure 8. (a) SEM image of the corroded 100% Al sample after pickling, (b)SEM image of the corroded surface of Al-13.0wt%AlN-1.0wt%Mg after pickling, (c) SEM Image of Al-6.5wt% AlN-0.5wt% Mg sample containing the corrosion products after 24 hours immersion in 0.05M NaOH solution.

It was observed that the mode of corrosion of the unreinforced Al sample, Figure 8 (a), was both by uniform corrosion on the entire surface and localized attack at some points leading to pitting corrosion as shown on the image. Figure 8(b), represents the sample Al-13.0wt% AlN-1.0wt% Mg. It was observed that the corrosion attack was selective: at the grain boundaries and on the aluminium grains while the secondary phase (AlN) remains almost undisturbed due to its high corrosion.

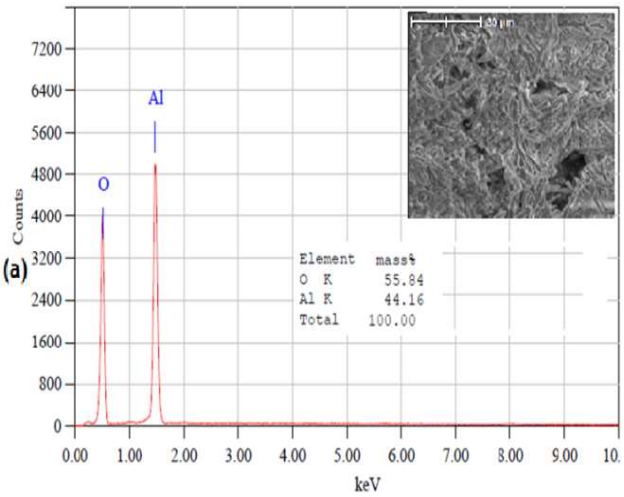


Figure 9. EDS Results of Corroded Surface of 100%Al sample after Pickling.

The EDS result of the 100%Alsample shown in Figure 9 revealed that the corroded surface contains 44.16%Al and 55.84%O. This suggest the presence of Al_2O_3 on the corroded surface

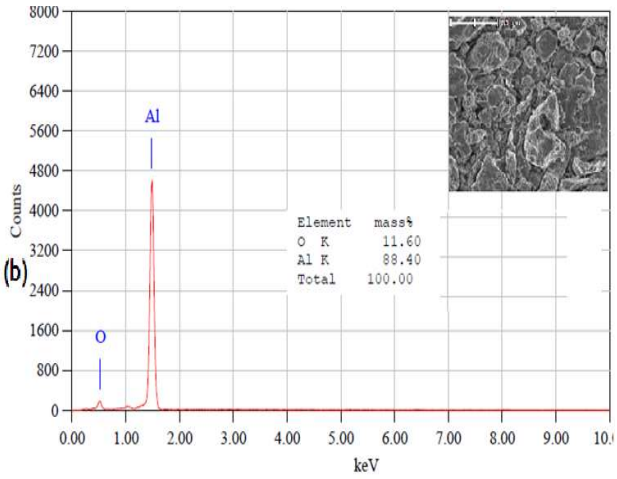


Figure 10.EDS Results of Al-13%AlN-1.0%Mg Sinter after Pickling Cleaning

In Figure 10, representing sample Al-13.0wt%-1.0wt%Mg, the EDS result gave the composition of a given portion on the sample as; 11.60%O and 88.40%Al. Comparing the amounts of oxygen on the unreinforced Al sample and that of sample, Al-13wt%AlN-1.0wt% Mg it shows that the latter has more corrosion resistance than the former considering the amounts of oxygen on its (the latter) surface as identified by the EDS result Total-Materia (2003).

The effects of weight fractions of the reinforcement and magnesium on corrosion rate are shown in Figure 11.

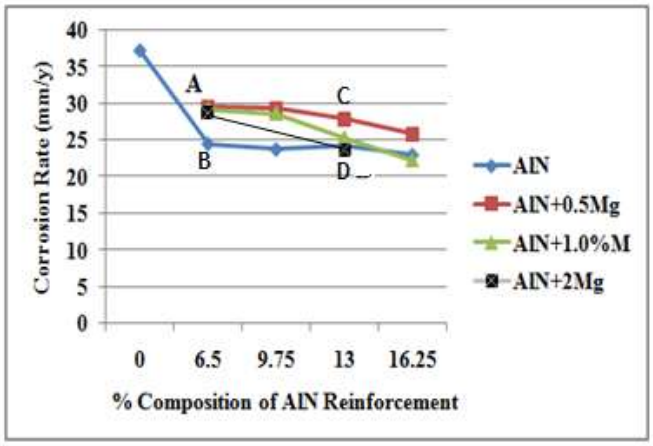


Figure 11: Effects of weight fractions of AlN and magnesium addition on the corrosion rate of the samples.

The results in Figure 11 show that the corrosion rate of the samples decreased sharply from 37.19mm/y in the unreinforced aluminium sample through 24.55mm/yr in the sample containing 6.5wt%AlN to 23.03 mm/yr in the sample containing 16.25wt%AlN. This means that the unreinforced aluminium sample (100%Al) recorded the highest value of corrosion rate (37.19mm/yr). The decrease in corrosion rate with the weight fraction of the secondary phase (AlN) was very small as observed by Abdoli, *et al.,* (2010). The reason for the insignificant reduction in the corrosion rate could be attributed to the fact that the secondary phase only occupiedan insignificant portion of the exposed surfaces. Higher weight fractions of the secondary phase than the ones used in this work could improvethe corrosion resistance of the composites significantly.

The effect of weight fractions of magnesium in the samples could be observed from points A to B and from points C to D in Figure 11 with the compositions Al-6.5wt%AlN and Al-13.0wt%AlN respectively. At these points;A and B or C and D containing the same amount of secondary phase in the samples, the trend in corrosion rate values with magnesium addition shows a decrease in values in the order 0.5<1.0<2.0wt%Mg. this means that the corrosion rate decreases with the amount of magnesium added in the samples. However, the sample containing Al-16.25wt%-1.0wt% Mg offered the best corrosion resistance as shown in Figure 11.

Comparing the samples containing magnesium with those without it, the results showed that the samples without Mg gave lower values of corrosion rates in composites containing between 6.5wt% and 13.0wt% AlN. In the samples containing 16.25wt% AlN, the corrosion rate of the sample containing 1.0wt% Mg was the lowest. This sample, therefore, offered the highest corrosion resistance of all the compositions tested.

4.0 Conclusion

From the above results and discussions, the following conclusions have been drawn:

- The result of the four-point probes test shows that the electrical conductivity values of the composites increased with both the amounts of reinforcement and magnesium added. The unreinforced aluminium sample recorded the lowest value of electrical conductivity while the sample with the compositionAl-16.25wt%AlN-1.0wt%Mg gave the highest value of electrical conductivity.

- The main corrosion products on the samples were $Al(OH)_3$, $Na_2Al_{11}O_{17}$ and $Na_7Al_3O_8$. The corrosion rate of the samples decreased with the weight fractions of AlN and Mg added. The influence of the weight fractions of AlN in the composite is more effective in reducing the corrosion rate of the samples than in those samples where Mg was added as a wetting agent. The sample containing 16.25wt%AlN-1.0% Mg offered the best corrosion resistance while the unreinforced aluminium sample corroded the most.

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