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EFFECTS OF MAGNESIUM ON PROPERTIES OF AlZrCe-Mg-Al_2O_3 NANOCOMPOSITES

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ABSTRACT

Aluminum alloy is one of the materials found in many applications, especially for electrical conductor materials. AlZrCe alloy reinforced by Al_2O_3 nanoparticles with Mg addition is proposed as one of the alternative materials to replace Aluminum Conductor Steel Reinforced (ACSR) as an aluminum conductor. Aluminum alloy Al-0.12%Zr-0.15%Ce as a master alloy was added with various weights of magnesium (Mg) from 2 to 5 wt% and was reinforced with 1.2% volume fraction of Al_2O_3 nanoparticles with particle sizes less than 80 nm. The molten metal matrix was blended with the reinforcement by a stirrer with a rotational speed of 500 rpm at a temperature of 750^{o}C in an argon gas environment and casted by gravity casting. The objective of this research was to investigate the effect of magnesium on microstructural changes, electrical conductivity, and mechanical properties, such as tensile strength and hardness of the composites. The microstructure observation results showed that the greater the Mg content in composites up to 5%, the smaller the grain size of the composite matrix, wherein the grain size of the composite without Mg is 28 μm, while the grain size of the composite with Mg of 2%, 3% and 5% are 27 μm, 17 μm and 9 μm respectively. Similarly, tensile strength and hardness increased with increasing levels of Mg to 5% where the addition of 5% Mg, the tensile strength increased from 106 to 204 MPa and hardness increased from 30 to 68 BHN. In contrast, the electrical conductivity sharply decreased, due to the addition of Mg in the composite with a gradient of reduction, to 2.74% IACS (International Annealed Copper Standard) for every increasing 1% Mg. In which the electrical conductivity of the composite without Mg is 55.1% IACS and after adding 5 wt% Mg, it decreased to 41.3% IACS.

Keywords: Al_2O_3; Aluminum zirconium cerium; Magnesium; Nanocomposites; Stir casting

1. INTRODUCTION

Conventionally, aluminum alloy has been applied mainly to the overhead conductor field, taking advantage of a density of 1/3 and a high conductivity of 2/3 in electrical conductivity compared with copper. From the viewpoint of the effectiveness of energy transfer, the lightweight aluminum alloy conductor is very effective. Nevertheless, the use of aluminum as an electrical conductor still needs to be optimized, especially for the properties required for a conductor wire. This has prompted many researchers to conduct research to improve the properties of the electrical conductivity, heat resistance and mechanical properties,

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such as the addition of 0.1%–0.3wt% cerium zirconium in pure aluminum (Zamroni, 1997). The addition of rare earth metals, such as cerium at 0.05wt% and 0.72wt% can increase electrical conductivity. The addition of zirconium can increase durability and lower electrical conductivity, but cerium additions will increase the electrical conductivity.

Other efforts needed to improve aluminum conductor behavior are to increase the mechanical properties. One effective way to improve the mechanical strength of the material is the use of nanoparticles as reinforcement in the aluminum matrix. It has been well understood that the presence of a dispersion of fine particles (<100 nm) in a metal matrix greatly improves creep resistance, though with only a small volume fraction <1% (Roohollah et al., 2010). Research about the addition of nanoparticles in aluminum alloys has been performed by several people, among those who have reported improvement in the mechanical properties of the AlZrCe by using Al_2O_3 nano-sized particles (Kirman et al., 2014). The achievement in increasing the strength of the composite with ceramic particles is influenced by improving the wetness of particles in the matrix. Increasing the wetness level of the particles in the matrix can be done by adding a wetting element, such as magnesium.

Broadly speaking, the addition of magnesium to the aluminum can increase the strength. Magnesium atoms may be used to substitute with aluminum atoms in the aluminum crystals that produce lattice distortions, which can hinder dislocation motion and reduce the dendrite arm spacing and smooth the grain of aluminum so that the mechanical properties are increased. The existence of magnesium in aluminum is often also considered to contribute to the formation of intermetallic compounds along with the impurities that are in aluminum, such as Mg2Si (Girisha et al., 2012).

The existence of magnesium also serves as a wetting agent of Al_2O_3 particles in the aluminum matrix so that the adhesion of the particle and the aluminum increases by increasing wettability. Good wettability is caused by the formation of $MgAl_2O_4$ (spinel) and MgO compound through reaction between Mg with Al and Al_2O_3 (Schultz et al., 2011). As a result, a good load transfer happens with the interface between the matrix and Al_2O_3 particles in order to obtain a high mechanical strength. By the presence of these compounds in the interface, the load transfer between the matrix and the particles becomes better and also the presence of porosity that is often found in the particle-matrix interface can be minimized.

Previous investigations where Al was reinforced by micro Al_2O_3 with content ranging from 20–50 wt-% showed a significant reduction in the Coefficient of Thermal Expansion (CTE) compared to unreinforced Al (Milos et al., 2011). Since the restriction effect of reinforcement particles causes CTE reduction, it is expected that using nanoparticles as reinforcements would even further reduce composite CTE. Moreover, the addition of Mg as a wetting agent to form spinel ($MgAl_2O_4$) with the reinforcement and matrix supposedly gives better thermal resistance because of better bonding between them.

The purpose of this paper is to investigate the effect of Mg addition in aluminum alloys, such as Al-0.12%Zr-0.15%Ce that are reinforced with 1.2 vf% nano-sized particles of Al_2O_3 based on mechanical, electrical, and thermal properties. The effect of Mg in the aluminum composites may improve the mechanical properties, but the effects of other properties, such as electrical and thermal properties need to be studied because these properties are important in aluminum, especially for aluminum as a conductor of electricity

2. EXPERIMENTAL

2.1. Starting Materials

The master alloy AlZrCe was first made by using pure Al, Al-5Zr and Al-10Ce supplied by PT Inalum and Hunan Jinlianxing Special Material Co. Ltd respectively. Pure aluminum was melted in a crucible at a temperature ranging from 750–800^{o}C and then it was decreased to 700^{o}C. During this temperature setting, Al-Zr and Al-Ce was introduced into the melt and then it was stirred to distribute all of the alloying elements evenly. It was then poured into an 800 gram ingot mold. Particles of Al_2O_3 <80 nm were added as a reinforcement of the composite and these were supplied by US Research Nanomaterials, Inc., Houston, USA. The chemical composition test of the master alloy AlZrCe was conducted by Optical Emission Spectroscopy (OES) and the results were as shown in Table 1.

Table 1 Chemical composition of AlZrCe alloy

Alloy material	Weight %					
	Al	Zr	Ce	Si	Fe	others
AlZrCe	98.30	0.12	0.15	0.39	0.88	0.18

2.2. Production of $AlZrCe/Mg/Al_2O_3$ Nanocomposites

The $AlZrCe/Mg/Al_2O_3$ nanocomposite was produced by the stir casting method with use of an apparatus as shown in Figure 1. An aluminum alloy AlZrCe that was reinforced with 1.2 Vf% Al_2O_3np was added with Mg as a wetting element, which varied from 2 to 5 wt%. The production process started with alloying Mg with the matrix and then feeding reinforcements into the matrix by inserting the particles into aluminum foil capsules before putting them in the aluminum alloy in the furnace. The melted aluminum alloy was degassed by inert argon gas and it was stirred with a rotational speed of 500 rpm at a temperature of 750°C for 2 to 3 minutes. Then the melted metal matrix composite was poured into a permanent tensile test mold (Figure 1) and then it was allowed to cool and solidify in the mold.

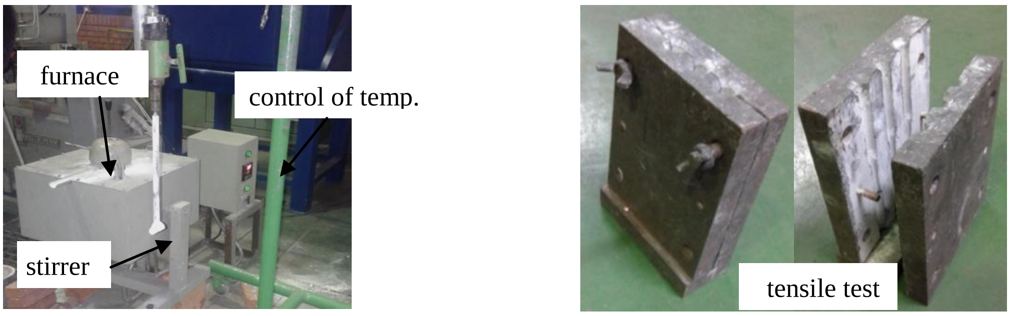


Figure 1 The experimental apparatus for producing the composites by the stir casting method and tensile test mold

2.3. Examination Methods

Three pieces of tensile specimens were prepared from each composition as shown in Figure 2. The dimensions of the tensile specimens were the gauge-length of 32 mm and a diameter of 6 mm. The tensile specimens were tested with a universal tensile testing machine Carl Schenck RME100 in accordance with the ASTM E8 standard. The hardness of the samples was measured using the macro hardness Brinnel by applying a load of 31.25 kg with a 2.5 mm diameter indenter and the load was applied on the sample for 20 seconds. The electrical conductivity test was conducted using the eddy current method with a frequency of 10kHz on the samples' surface. With this method, the electrical conductivity of the composite sample is determined by comparing the electrical conductivity of the pure aluminum that is known as 61% IACS. On the other hand, microstructural analysis was prepared by a metallography procedure, starting from grinding the specimens through 80, 120, 240, 500, 700, 1000, 1200 grit SiC papers followed by polishing with 6, 3, 1, ¼µm diamond pasta and etching with Keller's Reagent. The microstructures were obtained by viewing the samples at different magnification levels on an optical microscope and a Scanning Electron Microscope (SEM). Phases that formed in composites and changes in the crystal lattice of the aluminum were analyzed using the X-Ray Diffraction (XRD) test.

Figure 2 Tensile test specimens

3. RESULTS AND DISCUSSION

3.1. Microstructure of AlZrCe/Mg/Al_2O_3 Nanocomposites

Comparison of the composite grain size is shown in Figure 3 where the grain size of the composite without Mg is 28 µm while for composites by weight the Mg content of 2%, 3% and 5% are 27 µm, 17 µm and 9 µm respectively.

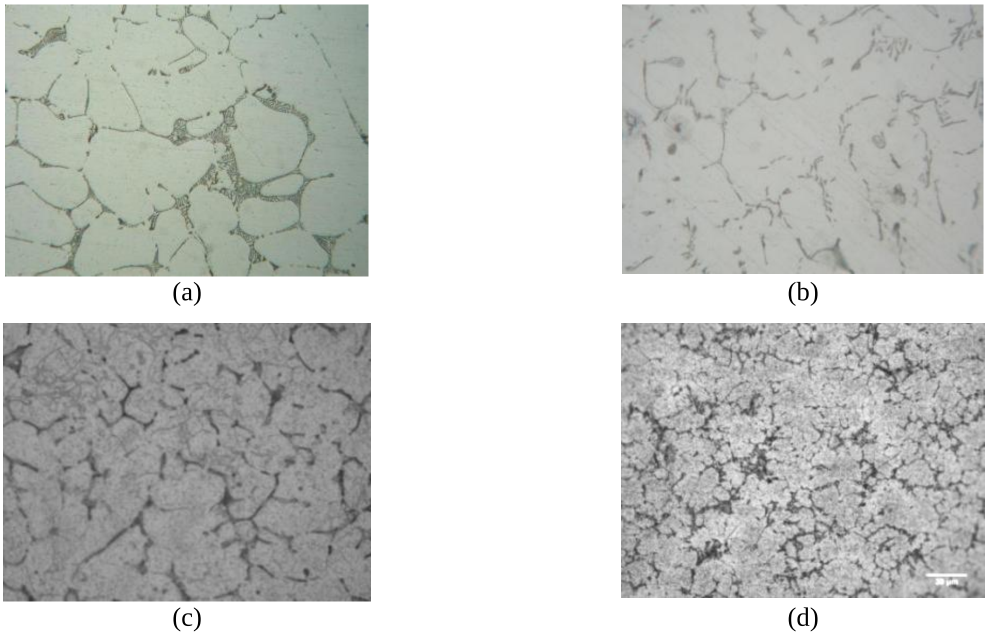


Figure 3 Microstructures of composites AlZrCe/Mg/Al_2O_3 with various weight contents of Mg: (a) without Mg; (b) 2%wt Mg; (c) 3%wt Mg; and (d) 5%wt Mg. Etching with Keller's Reagent

Therefore, the higher the Mg contents in the composite, the smaller the grain size. These results are consistent with previous studies (Girisha et al., 2012) that Mg can reduce the size of grains of aluminum. This result is also consistent with the theory of the Restriction Growth Factor (GRF) in which the segregation power of the Mg element in the aluminum alloy can be predicted by knowing the value of the growth-restriction parameter Q of Mg in the aluminum (Chandrashekar et al., 2009) by using Equation 1 as follows:

$$Q = \Sigma\ m_i(k_o - 1).c_o \tag{1}$$

where c_o the average bulk solute content in wt %, m_i is the gradient of the liquidus line, k_o is the equilibrium partition coefficient. Values of m and k for Mg element in aluminum are -6.2 and 0.51 respectively, as can be seen in Table 2. The calculation results of the Q value is calculated by using Equation 1 for the Mg contents of 2 wt%, 3 wt% and 5 wt% are 6.1, 9.1, and 15.2 respectively. Thus, it can be predicted that the greater Mg content in aluminum, the smaller grain size. This occurs because growth-restriction parameter Q is inversely proportional to the growth rate. The segregation process of Mg will be at the site of the nucleation of the grains.

Table 2 Values for m, k, $(k_i\text{-}1)m_i$ and the concentration of alloy that can be dissolved in aluminum (St. John & Easton, 1999)

Element	k_i	m_i	$(k_i\text{-}1)m_i$	Max. Concentration (wt%)
Ti	~9.0	30.7	245.6	15.00
Ta	2.5	70.0	105.0	~0.10
V	4.0	10.0	30.0	~0.10
Hf	2.4	8.0	11.2	~0.50
Mo	2.5	5.0	7.5	0.10
Zr	2.5	4.5	6.5	~0.11
Nb	1.5	13.3	6.6	~0.15
Si	0.11	-6.6	5.9	~12.60
Cr	2.0	3.5	3.5	~0.40
Ni	0.007	-3.3	3.3	~6.00
Mg	0.51	-6.2	3.0	~3.40
Fe	0.02	-3.0	2.9	~1.80
Cu	0.17	-3.4	2.8	33.20
Mn	0.94	-1.6	0.1	1.90

3.2. Tensile Strength of AlZrCe/Mg/Al_2O_3 Nanocomposites

The mechanical properties of the nanocomposites with 1.2 Vf% of Al_2O_3 are shown in Figures 4a, 4b, and 4c. The tensile strength and the hardness continuously rise by increasing the content of the Mg up to 5 wt%. The addition of the Mg elements into the composites has significantly improved tensile strength and hardness in which the tensile strength increased 92% and the hardness increased 127%. The improvement of strength was expected, due to an improvement of the wettability of the Al_2O_3 particles in the aluminum matrix. High level interface wettability causes the particles and the matrix to transfer the external load better and Orowan strengthening mechanisms (Jamaati et al., 2010) will work well where the particles in the field of the dislocation can inhibit the occurrence of movement. The increasing strength factor also is affected by grain refinement as shown in Figure 1. In contrast, elongation of composites continuously decreases when the Mg content increases. The decrease in elongation was caused by the bonding strength of the particles to the metal stronger than the composites without Mg content. Increased strength and hardness of the composite is also affected by grain refinement as shown in Figure 4, where the strength of the aluminum alloy rises when the finer grain size occurs.

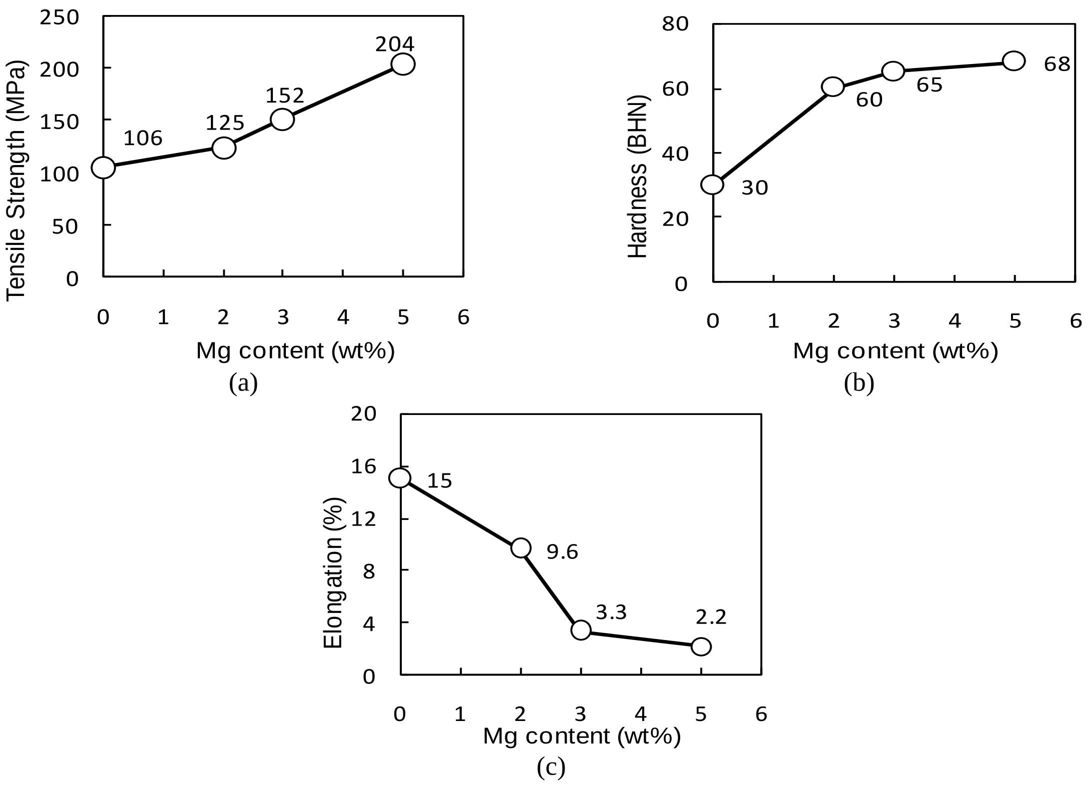


Figure 4 Mechanical and electrical properties of Al-Zr-Ce-Mg/Al_2O_3 nanocomposites: (a) tensile strength; (b) hardness; and (c) elongation

3.3. Electrical Properties of AlZrCe/Mg/Al_2O_3 Nanocomposites

Figure 5 shows that the electrical conductivity decreased sharply, due to the presence of Mg in the composite AlZrCe/1.2% Al_2O_3 up to 5 wt% while the gradient of reduction is 2.74% IACS for every increase 1 wt% of Mg. The use of nanoscale reinforcement particles can minimize the electrical conductivity decrease (Weber et al., 2003). But due to the addition of the Mg element, which increases the wettability of the particles in the matrix and results in a significant reduction of the value of the electrical conductivity. The decrease of conductivity due to Mg has a high electrical resistivity and is spread evenly in the aluminum matrix that caused distortion of the crystal lattice so that the movement of electrons becomes impeded. The XRD test results on composite AlZrCe/5%Mg/Al_2O_3 indicate that distortion of the crystal lattice of aluminum has occurred, which is characterized by the shift of a diffraction peak of aluminum by -2.50 2theta value as shown in Table 3.

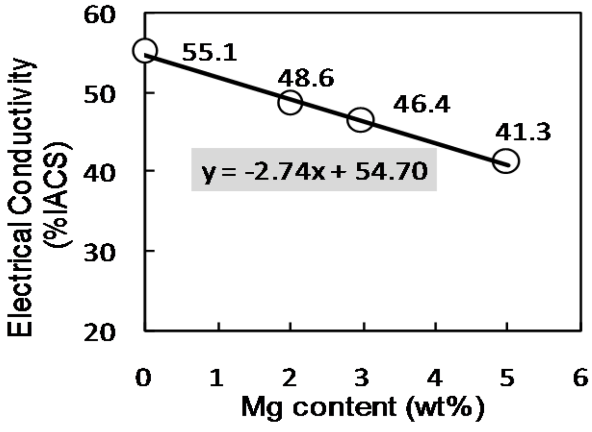
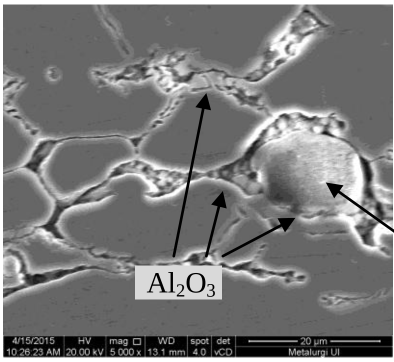


Figure 5 Electrical conductivity of Al-Zr-Ce-Mg/Al_2O_3 nanocomposites

Moreover, the smaller grain size has the potential to degrade the electrical conductivity because at the grain boundaries there are a lot of Al_2O_3 particles and impurities, when combined together with Mg to form intermetallic compounds at the grain boundaries as shown in Table 3 and Figure 6. The presence of impurities at the grain boundary may impede the movement of electrons when passing through the grain boundaries (Mrowka-Nowotnik et al., 2007).

Table 3 Analysis of XRD test results of composite AlZrCe/5%wt Mg/1.2%Vf Al_2O_3 by using *software* "XPert Highscore Plus"

Ref. Code	Score	Compound Name	Displacement (°2Th.)	Scale Factor	Chemical Formula
01-089-4037	65	Aluminum, syn	-0.250	1.056	Al
00-004-0877	18	Alumina	0.311	0.019	$Al_2 O_3$
00-001-1157	13	Spinel	-0.199	0.012	$Mg Al_2 O_4$
00-034-0458	64	Magnesium Silicon	-0.015	0.020	$Mg_2 Si$
00-001-1265	25	Iron Aluminum	-0.176	0.285	$Fe Al_3$
00-007-0135	38	Cerium Iron	-0.721	0.005	$Ce Fe_2$
00-007-0142	9	Cerium Iron	0.214	0.034	$Ce Fe_5$
03-065-0674	21	Aluminum Zirconium	0.104	0.432	$Al_3 Zr$
00-001-0649	31	Quartz	0.475	0.014	$Si O_2$



Element	Wt%	At%
O	18.71	27.88
Mg	04.59	04.50
Al	72.82	64.33
Si	03.88	03.29

Element	Wt%	At%
O	45.49	58.37
Mg	01.73	01.46
Al	52.79	40.17

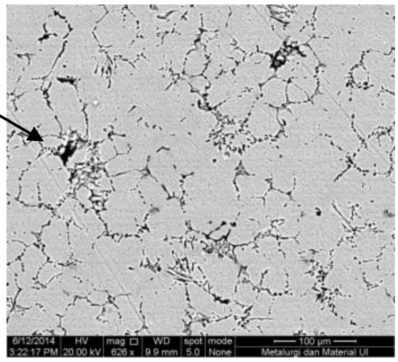


Figure 6 The result of SEM/EDS showed that Al_2O_3 particles, impurity Si and Mg exist at grain boundaries

3.4. Thermal Expansion of AlZrCe/Mg/Al_2O_3 Nanocomposites

The thermal expansion of the nanocomposites was tested using a dilatometer in a range of 150-350°C. The effect of adding Mg in the composite AlZrCeMg/Al_2O_3 on the thermal properties is shown in Figure 7, which indicates that with an increase in the number of levels of Mg in the composite of up to 5 wt%, the coefficient of thermal expansion (CTE) composites increased with the gradient of 0.266, thereby, increasing the CTE results of improved wettability of nanoparticles in the matrix. This result caused a restriction effect of nanoparticles to the matrix, which is higher than without Mg addition, due to the good bonding strength of the nanoparticles and the matrix so the response by the composite heat is faster. In addition, the presence of Al_2O_3 nanoparticles in the composite with a high CTE in the aluminum, where the expansion of composite when the CTE owned by Al2O3 was much less than pure aluminum i.e., 23.1×10^{-6} and 8.1×10^{-6} m/m.K respectively (Amirkhanlao, 2011), which will restrain the contractions of aluminum to expand when the heat is exposed to the nanocomposites.

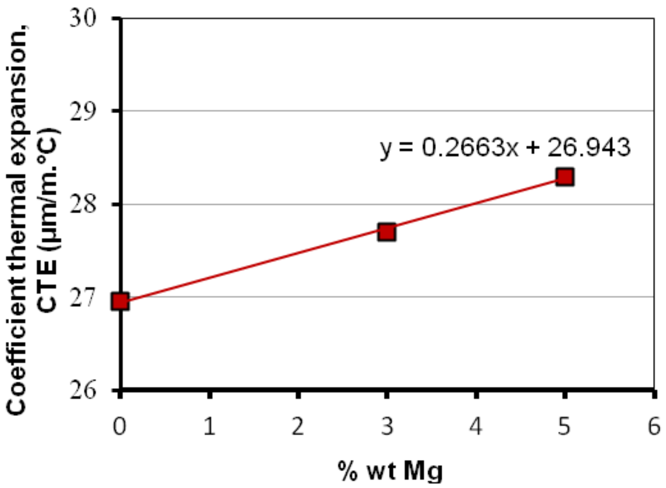


Figure 7 Effect of adding Mg to the thermal expansion properties of as-cast composite AlZrCeMg/Al_2O_3

4. CONCLUSION

AlZrCe/Mg/Al_2O_3 nanocomposites were modified by adding various weights of Mg ranging from 2–5%. The microstructure observation result shows that the greater the Mg content in the composite of up to 5%, the grain size is smaller. Tensile strength and hardness are always increased by increasing the Mg content up to 5%, whereas elongation and electrical conductivity were continuously decreased by increasing the Mg content. The addition of 5% Mg increased tensile strength 92% and hardness 127%. The electrical conductivity was sharply decreased, due to the addition of Mg in the composite with a gradient of reduction being 2.74% IACS for every increase of 1% Mg content.

5. ACKNOWLEDGEMENT

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