International Journal of Technology (2016) 3: 383-391
ISSN 2086-9614

CHARACTERIZATION OF Al-0.12Zr-0.15Ce REINFORCED BY AL_2O_{3np} AS COMPOSITES CONDUCTOR

Anne Zulfia[1*], Fadli Robby[1], Kirman[1,2], Agus Sukarto[3]

[1] *Department of Metallurgy and Materials, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[2] *Technology Center for Strength of Structures. Agency of the Assessment and Application of Technology (BPPT), Building 220, Puspiptek, South Tangerang 15314, Indonesia*
[3] *Research Center for Physics. P2F LIPI, Kawasan Puspiptek, Serpong, Tangerang 15314, Indonesia*

(Received: December 2015 / Revised: January 2016 / Accepted: February 2016)

ABSTRACT

Aluminum, as a conductor material, has long been used for high-voltage overhead transmission lines due to its economic value and high electrical conductivity. By adding Al_2O_{3np} and alloying elements such as zirconium (Zr), cerium (Ce), and magnesium (Mg), aluminum's strength and performance could be improved without compromising too much of its electrical conductivity. The focus of this research was to investigate the mechanical, electrical properties, and microstructure of Al-0.12%Zr-0.15%Ce-5%Mg, reinforced with different volume fractions (from 0.5 to 1.5%) of Al_2O_3 nano particles, using the stir casting method. The tensile strength of the composite was improved by up to 1.2 vf-% in alumina, and decreased with further addition due to clustering and pores, while elongation was reduced with when increasing the reinforcement. It was found that the electrical conductivity of the composite generally decreased with the addition of reinforcement. The microstructure observations showed that the composites yielded finer grains and more pores than the unreinforced alloy, with 1.2vf-% of reinforcement having the finest grain. The electrical conductivity of the composite was 44% IACS, which is still lower than that of the unreinforced alloy.

Keywords: Al_2O_3 nanoparticles; Electrical conductivity; Master alloy Al-Zr-Ce; Stir casting; Tensile strength

1. INTRODUCTION

Aluminum wire is used as a high voltage electrical conductor in transmission lines. This is due to its low density, high electrical conductivity, and relatively low cost, which covers some of the requirements for such an application in which conventional Al still falls short (Eugene et al., 1989). The development of aluminum conductors is now trending in the direction of a metal matrix composite with Al-Zr-Ce that is reinforced with Al_2O_3 nanoparticles; this is designed to increase the strength of the aluminum wire, while not having a significantly adverse impact on its electrical conductivity. Zr and Ce have been proven to give better high temperature resistance, and to have the ability to increase electrical conductance, in several studies (Sato et al., 1981; Horikosh et al., 2006; Gunawan, 2000). However, the addition of Zr to other impurities could possibly reduce the electrical conductivity of Al by distorting its atomic lattice; therefore, Zr should be added in small amounts (Paul Springer, 2006). The addition of rare-

---

*Corresponding author's email: anne@metal.ui.ac.id, Tel. +62-21-7863510, Fax. +62-21-7872350
Permalink/DOI: http://dx.doi.org/10.14716/ijtech.v7i3.2866

earth metals such as cerium (Ce) has been reported to compensate for that reduction by forming a meta stable compound and second phase such as $FeAl_3$ or Ce_3Si_2. A study by Pengfei et al. (2006) stated that rare-earth metals such as Ce form intermetallic compounds with impurities in Al and segregate at the grain boundary, thus altering the distribution of impurities and improving electrical conductivity. The addition of Ce also functions as a grain refinement, so that the mechanical properties can be improved. Aluminum, alloyed with zirconium and cerium, promises improvement that is suitable for the needs of electrical applications; however, the development of such alloys is still limited.

The strengthening effect when using Al_2O_3 nano particles is greater than when using microparticles, which cause a reduction in electrical conductivity. This hypothesis is supported by Sajjadi et al. (2006), who determined that the addition of 1-4% of Al_2O_3 nanoparticles to an A356-based composite could enhance the tensile strength, hardness, and compressive strength, unlike the addition of Al_2O_3 microparticles with the same content. This is due to the shorter distance between particles in the matrix, which could amplify its strengthening mechanisms; these are, namely, good load transfer and CTE mismatch between matrix and reinforcement, orowan strengthening, grain refinement, and Zener pinning effect, according to Casati and Vedani (2014).

In this study, the effect of reinforcing Al_2O_3 nanoparticles content in Al-Zr-Ce/Al_2O_3 nano composite with the addition of 5 wt-% Mg through the stir casting route is characterized as a way of determining its mechanical and electrical properties, along with microstructural observation, in order to obtain the optimum content of reinforcement that yields balance in the properties of an aluminum conductor.

2. EXPERIMENTAL METHOD

The material used for fabricating the nano composite was Al-0.12% Zr- 0.15% Ce master alloy, which was produced using pure Al, Al-5Zr, and Al-10Ce, and melted and casted at a temperature of 750-800^oC. We also used α-Al_2O_3 with a size of approximately 80 nm, supplied by US Nano Materials Research Inc; we de-agglomerated it by mixing it with 3% stearic acid and crushing it with a mortar and stamper. The reinforcement content was varied from 0.5 to 1.5 vol. fraction and 5 wt-%. Mg was added to molten Al. The master alloy was melted at 850^oC for two hours. After dross on the surface of the melt was removed, 5 wt-%Mg was added to the molten Al, then stirred and degassed using argon for one minute. The preheated Al_2O_3 was then introduced to the melt, followed by manual stirring at a speed of 500 rpm and Ar degassing for three minutes. The melt was poured into a tensile testing and plate mold. The chemical composition of the nano composite was tested using Oxford Instrument PMI Pro Optical Emission Spectroscopy (OES) and PW 2400 X-Ray Spectrometer X-Ray Diffraction (XRD). Tensile testing of the nano composite was carried out using a Gotech AI-7000 LA 10, in accordance with ASTM E8M-09. Each variable of the composite was tested using three specimens. A Mini Pasce Eddy current was used to measure the electrical conductivity of the composite, in accordance with ASTM E1004. The frequency used for the measurement was 10 kHz, and the samples' dimensions were 30×30×10 mm. Microstructural observation was done using an Olympus BX41M-LED optical microscope and an Inspect F50 FE-SEM. Metallography preparation of the samples was carried out by grinding using 80#–1200# emery paper, followed by polishing using TiO_2; it was then etched for about 30–45 seconds with Keller's Reagent (2ml HF, 5 ml HNO_3, 3 ml HCl, and 190 ml aquadest) being used as an etching reagent.

3. RESULTS AND DISCUSSIONS

3.1. Chemical Composition of Al-Zr-Ce /Al_2O_{3np} Composite

The following chemical composition test results of the Al-Zr-Ce master alloy and nano composites were analysed by Optical Emission Spectroscopy (OES), as shown in Table 1. The Mg and Zr content could be considered as close to the designed alloy, at 5wt-% and 0.12wt-%, respectively. The Ce content, which might be related to instrument limitation to detect rare earth inner elements, experienced a fading effect caused by oxidation.

Table 1 Chemical composition of nano composites

(%Vf) Al_2O_3	Chemical composition *wt*%						
	Al	Si	Fe	Zr	Ce	Mg	bal
0	98.3	0.393	0.878	0.12	0.0068	0	0.3022
0.7	93.3	0.509	0.774	0.0869	0.0071	5.1	0.223
1	92.6	0.446	0.884	0.08	0.0053	5.87	0.1147
1.5	92.4	0.462	0.9	0.0814	0.0072	5.94	0.2094

3.2. Microstructure of Al-Zr-Ce /Al_2O_{3np} Composite

The microstructure of the Al-Zr-Ce/Al_2O_3 nanocomposite is shown in Figure 1. Based on observations, further addition of reinforcement reduced the size of grains. It was also seen that 1.2% Al_2O_3, in a nanocomposite with 5% Mg addition, produced the finest grain compared to the others. A reduction in grain size was also found by other investigators when increasing Al_2O_3 (Surapa et al., 2003; Zhou et al., 2009). It is seen that increasing the volume fraction of Al_2O_3 generally decreases the precipitate distance. The reduction in the distance between the precipitates indicates the occurrence of grain refinement in the matrix, as the precipitates grow in the grain boundaries. Refinement is caused by the presence of Al_2O_3 in the matrix, which can act as both an instigator of grain formation and an inhibitor of grain growth. Therefore, the more alumina are added, the smaller the grain growth will be in general (Schultz et al., 2011). Between grains, there are presumably Mg_2Si intermetallics (white arrows) that come from the reaction between Mg and Si in the material with the morphology of Chinese script, according to Adams (2004) and Mrówka et al. (2007).

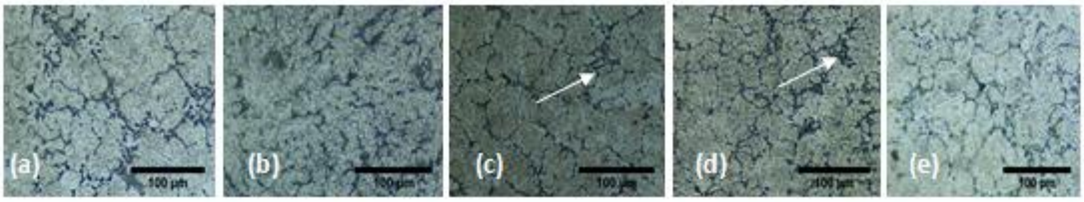


Figure 1 Microstructural observation of Al-Zr-Ce nanocomposite with 5% Mg and various Al_2O_3 content: (a) 0.5 vf-%; (b) 0.7 vf-%; (c) 1.0-vf%; (d) 1.2 vf-%; (e) 1.5 vf-%

Upon further observation under higher magnification, it was seen that some phases were formed in nano composites, as shown in Figure 2; the chemical composition of each phase is found in Table 2. Spot 1 is a matrix, while spot 2 is presumably an Mg_2Si intermetallic that came from the reaction between Mg and Si in the matrix with the morphology of Chinese script. The white phases on spots 3 and 4 are asummed to be Al_3Fe and Ce Fe_5, formed in the matrix. In this phase, the concentrate of Fe and Ce was relatively high compared to other phases; therefore, the precipitates dispersed between not only Al and Fe, but Al and Ce due to Ce, have a high electron afinity as well as with Fe.

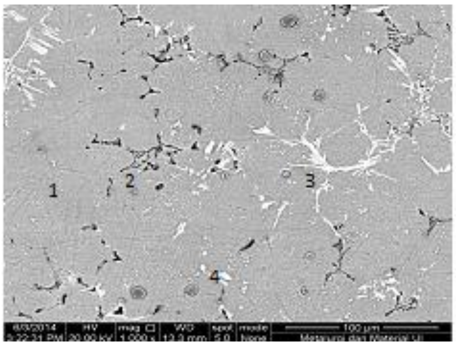


Figure 2 Microstructural observation of Al-Zr-Ce nanocomposite with 5% Mg and various Al_2O_3 content: (a) 0.5 vf-%; (b) 0.7 vf-%; (c) 1.0-vf%; (d) 1.2 vf-%; (e) 1.5 vf-%

Table 2 Chemical composition analyzed by EDS

Point	Chemical Compositon (wt%)						
	O	Mg	Al	Si	Zr	Ce	Fe
1	0.78	5.47	90.67	0.15	2.40	0.33	0.21
2	3.87	6.26	80.59	6.90	1.41	0.73	0.24
3	1.74	4.77	81.85	-	2.04	0.44	9.15
4	2.31	2.21	70.76	-	1.54	2.86	20.32

3.3. Tensile Strength, Electrical Properties, and CTE of Al-Zr-Ce/Al_2O_{3np} Nanocomposite

The effect of Al_2O_3np on tensile strength and elongation of nanocomposites is shown in Figure 3a. The maximum UTS was found at 1.2 vf-% Al_2O_3, which reached 204 MPa. The increase in the tensile strength of nanocomposites with the addition of Al_2O_3 nanoparticles was caused by dislocation motion impediment and was dispersive of Al_2O_3np. The wettability of composites with 5wt-% Mg was mainly dominated by $MgAl_2O_4$, but it seemed that the latter had the chance to form more interfacial reactions with reinforcement. Further addition of reinforcement caused a reduction in strength that can be attributed to possible agglomeration/clustering and pores inside the nanocomposite, which is a favored site for crack nucleation (Toshiyuki et al., 2006).

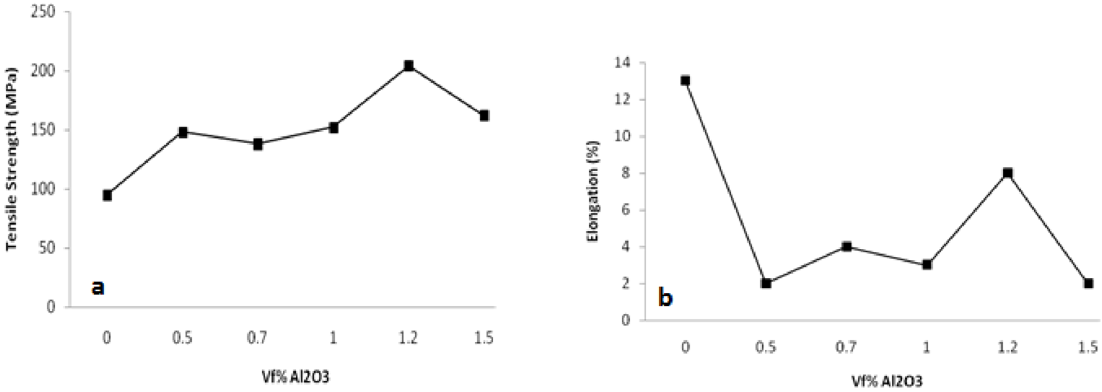


Figure 3 Effect of Vf% Al_2O_3 on the mechanical properties of AlZrCe/Al_2O_3 nano composites: (a) tensile strength; and (b) elongation

The elongation of the nanocomposite with 5 wt-% Mg and various Al_2O_3 nanoparticles content is shown in Figure 3b. Elongation of the nanocomposite with 5 wt-% Mg addition continued to rise to its peak reinforcement content (1.2%), before falling with further addition. The nanocomposite with 0.5 vf-% Al_2O_3 had a low elongation, which could be related to increased formation of Mg_2Si intermetallic compound, since it had a negligible amount of reinforcement. It seemed that the wettability of Al_2O_3 with 5wt-% Mg addition was improved by further interfacial reactions, and could withstand the addition of reinforcement up to 1.2vf%, resulting in better distribution of nanoparticles in the matrix and an ultimate refinement of the grain (Kirman et al., 2015).

Electrical conductivity that was observed as using an eddy current is shown in Figure 4a. It can be seen that the conductivity of the nanocomposites significantly declined from as-cast Al-Zr-Ce to Al, reinforced by Al_2O_3np. A foreign solute element such as Mg in Al was presented as a source of electron distortion. In addition, the possible uneven redistribution and fading of cerium could not dispensate the reduction of electrical conductivity caused by impurities in the matrix. The results are also in accordance with Weber et al. (2003), who reported that the addition of Al_2O_3 content of non-conductors would decrease the electrical properties of aluminum matrix composites. The electrical conductivity can be maintained, so as not to fall in value when adding cerium to aluminum. Peng et al. (2006) explained that the addition of rare earth elements such as cerium and tantalum increases the electrical conductivity of pure aluminum. This is caused by a decrease in the solubility of impurities, such as silicon and iron, in bulk aluminum, which leads it to have a high resistivity. Cerium has a sufficiently high affinity with impurities such as Fe and Si to establish an intermetallic phase with the soluble impurities in aluminium. The small size of the grain also affects the reduction in conductivity, as moving electrons have great difficulty in passing through the grain boundaries (Kirman et al., 2014). This means that the electrical conduction is obstructed, which leads to an increase in resistance. If the value of electrical resistance increases, the electrical conductivity will decrease.

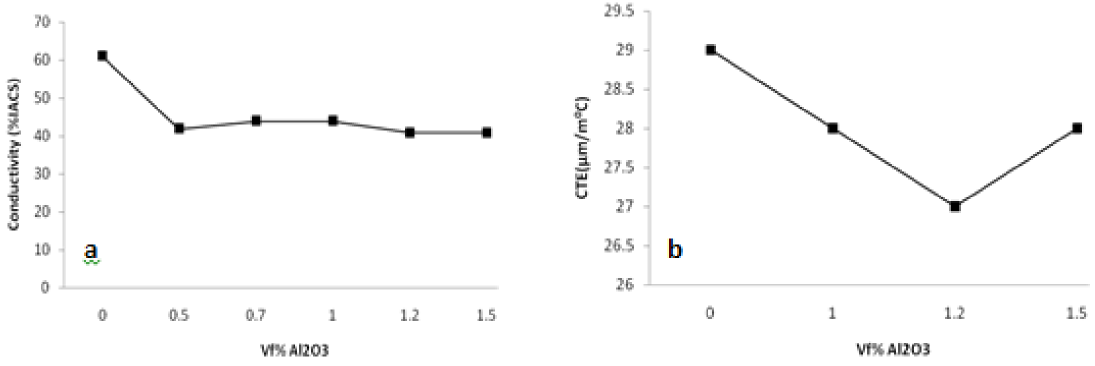


Figure 4 Effect of Vf% Al_2O_3 on electrical conductivity: (a) and coefficient of thermal expansion/CTE; (b) of AlZrCe/Al_2O_3 nano composites

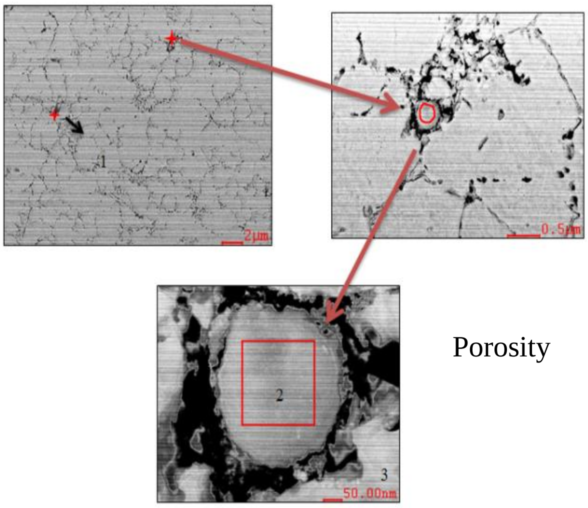
The coefficient of thermal expansion (CTE) is shown in Figure 4b. It is observed that with the addition of Al_2O_3, the expansion limitation effect should have been amplified; however, the 0.5 vf-% content was the exception as it had the lowest value. When increasing the amount of alumina particles, the coefficient thermal expansion value of the composite decreased in the presence of alumina, which has a low CTE and more precipitates in the Al matrix. With a refined grain, the material is actually more prone to expansion, but the precipitates that formed at the grain boundaries prevented this.

The addition of alumina also increases the value of CTE, as it leads to the formation of pores at the interface. The pore interface area, and the existence of these pores, causes the composite to more easily expand and enhance the value of CTE. Therefore, the rise and fall in the value of CTE is determined by whichever is the dominant factor: a large amount of precipitates in the presence of alumina, or a large amount of porosity. In our test, the results showed, in general, the occurrence of a reduction in CTE. This shows that the influence of the amounts of alumina and precipitates is more dominant than the effect of porosity. However, the test result data also showed an increased value of conductivity from a volume fraction of 1.2% to 1.5% Al_2O_3. This shows that with a volume fraction of 1.5%, the impact of porosity is more dominant than the effect of the addition of alumina and the amount of precipitates, compared with the 1.2% volume fraction of Al_2O_3. In contrast, Al_2O_3 can act to restrain the increasing heat, as its coefficient thermal is very low (7.1μm/m°C) when compared to that aluminum, which is about 25.5 μm/m°C. The small grain size can easily affect the material in terms of expansion; however, if there are many precipitates in the grain boundaries, the precipitates will restrain the thermal expansion with a constriction of the sliding of grain boundaries (Yi et al., 2007; Zhoe et al., 2009).

In their application, a decrease and increase in the value of CTE in this composite were not actually that significant, because the difference value was still below 1 μm/m°C. The CTE values obtained were still much greater than the value of the CTE of pure aluminum (25 μm/m°C). Both of these are caused by the existence of pores, which are difficult to control; these pores cause the material to more easily expand than a solid material with heat energy and the same volume.

3.4. Interface Area between Matrix and Reinforcement

The interface area was investigated by FESEM linked to EDS, as shown in Figure 5 and Table 3. It was observed that Al_2O_3 was not well dispersed, because the size of Al_2O_3 was shown to be above 100 nm due to agglomerate, whereas the desired size is about 80 nm. It seems that the local interface between the matrix and reinforcement was not effective, because the Al_2O_3 particles were not attached directly to the matrix and remained as pores. These pores certainly adversely affected the tensile strength, elongation, and conductivity, as well as the CTE of the nano composite.



Porosity

Figure 5 Interface area between Al matrix and Al_2O_3np in Al-Zr-Ce composites system

The Spot 1 content of Al, Mg, and Si is assumed to be an aluminum matrix; the oxygen indicates the presence of oxide compound, along with aluminum and Chinese script of Mg_2Si. Spot 2 is the particles content of O, Al, Mg, and Si, possibly making it Al_2O_3. The Spot 3 content of O, Al, Mg, and Si, as well as possibly Al_2O_3, had already reacted to form $MgAl_2O_4$ and impurities. The Chinese script of AlSi was also detected in the interface area.

Table 3 Chemical composition analysed by EDS

Point	Chemical Compositon (wt%)			
	O	Mg	Al	Si
1	18.71	4.59	72.82	3.88
2	27.11	6.02	61.68	5.19
3	15.09	4.66	61.25	19.00

During solidification, the reinforcement particle acts as a barrier to solute diffusion ahead of the liquid solid interface, and the growing solid phase will avoid the reinforcement in the same way that two growing dendrites avoid one another. The individual particles may be pushed by the moving solid-liquid interface into the last freezing inter-dendritic regions, or the growing cell may capture them. For small reinforcement particles, these particles will generally push towards freezing; the points forming grains and particles will then strengthen due to the principle of grain refinement (Jasmi, 1999). Nano-size particles will cause the particle to offer a strengthening effect with a grain refinement mechanism. The addition of nano-size particles into a bulk matrix amounts to very little in volume fraction, because they will easily be agglomerated, and dispersion is highly unlikely to occur in a large volume fraction (Sajjadi et al., 2011). The agglomeration may occur during the stirring motion, during which time the particles could coalesce with each other; due to the low temperature of reinforcement preheating (500^oC); or from an unreliable de-agglomeration process, which causes a lack of impact force and time in order to reduce the size of nanoparticles. A more effective method, using a ball mill with a longer time, high impact force, and higher preheating temperature can be employed in order to attain better distribution and prevent agglomeration of reinforcement (Rajkovic et al., 2008).

4. CONCLUSION

The tensile strength and elongation of composites Al-Zr-Ce was improved with the addition of 1.2 Vf% Al_2O_3np, then declined with further addition of the reinforcement. The Al_2O_3np resulted in a fine grain size of the matrix, as well as alloying elements such as Zr and Ce. The electrical conductivity was relatively stable with the addition of Al_2O_3np up to 1.5 Vf%, possessing IACS of approximately 44%, but was lower than Al when unreinforced. The addition of Al_2O_3 and Mg decreased the value of CTE composite, but the presence of porosity increased the value of CTE.

5. ACKNOWLEDGMENT

Authors would like to thanks to Higher Education, Ministry of National Education, Republic of Indonesia for financial support under Hibah Desentralisasi PUPT, 2013 with contract no. 2385/H2.R12/ HKP.0500/2013.

6. REFERENCES

Adams, B.L., 2004. *ASM Handboook Vol. 9: Metallography and Microstructures*. ASM International publisher, USA

Casati, R., Vedani, M., 2004. Metal Matrix Composites Reinforced by Nano-particles - A Review. *Metals*, Volume 4, pp. 65–83

Eugene, W.G., 1989. *Aluminum Electric Conductor Handbook Third Edition, Vol. 3*. Aluminum Association Publication

Gunawan, 2000. *Effect of Zirconium and Lanthanum Addition on Electrical Conductivity and Heat Resistance of Aluminum Conductor Wire*. Master Thesis, *Material Science*, Universitas Indonesia

Horikoshi, T., Kuroda, H., Shimizu, M., Aoyama, S., 2006. Development of Aluminum Alloy Conductor with High Electrical Conductivity and Controlled Tensile Strength and Elongation. *Hitachi Cable Review*, Volume 25, pp. 18–21

Jasmi, H., 1999. *The Production of Metal Matrix Composites using the Stir Casting Technique in Mechanical and Manufacturing Engineering*, Thesis, Dublin City University, Ireland

Kirman, M, Panji, M., Zulfia, A., 2014. Characteristics of AlZrCe-Al_2O_3 Nanocomposites Produced by Stir Casting Method as an Alternative Material for Electrical Applications. *Advanced Science Letters*, Volume 20, pp. 2271–2274

Kirman, M., 2015. *Fabrication and Characterisation of Metal Matrix Composites AlZrCe Reinforced by Al_2O_3(np) through Stir Casting Route*. Ph.D. Thesis, Department of Metallurgy and Materials, Faculty of Engineering, Universitas Indonesia

Li, P., Wu, Z., Wan, Y., 2006. Effect of Cerium on Mechanical Performance and Electrical Conductivity of Aluminium Rod for Electrical Purpose. *Journal of Rare Earths*, Volume 24, pp. 355–357

Mazahery, A., Abdizadeh, H., Baharvandi, H.R., 2009. Development of High Performance A356/Nano-Al_2O_3 Composites. *Mat. Sci. Eng A*, Volume 518, pp. 61–64

Mrówka, G., Nowotnik, J.S, Wierzbiñska, M., 2007. Intermetallic Phase Particles in 6082 Aluminium Alloy. *Materials Science and Engineering*, Volume 28, pp. 69–76

Paul Springer, P.D.C., 2006. *Al-Zr Alloy Strand for ACCR Conductor Experimental Measurement of Resistance Temperature Coefficient*. National Electric Energy Testing, Research & Applications Center

Rajkovic, V., Bozic, D., Jovanovic, M.T., 2008. Properties of Copper Matrix Reinforced with Nano- and Micro-Sized Al_2O_3 Particles. *Journal of Alloys and Comp*. Volume 459, pp. 177–184

Sajjadi, S.A, Behad, N., Mohammad, R.T., 2011. Reinforcement of Microstructure and Improvement of Mechanical Properties of Al/Al_2O_3 Cast Composite by Accumulative Roll Bonding Process. *Material Science and Engineering*, Volume 528, pp. 2548–2553

Sajjadi, S.A, Ezatpour, H.R, Parizi, M.T., 2006. Comparison of Microstructure and Mechanical Properties of A356 alloy/Al_2O_3 Composites Fabricated by Stir and Compo-casting Processes. *Materials and Design*, Volume 34, pp. 106–111

Sato, K., Yamauchi, K., Hanaki, Y., Kondo, T., Yokota, M., 1981. *U.S. Patent No. 4,402,763*. Washington, DC: U.S. Patent and Trademark Office

Schultz, B.F., Rohatgi, P.K., 2011. Microstructure and Hardness of Al_2O_3 Nanoparticle Reinforced Al–Mg Composites Fabricated by Reactive Wetting and Stir Mixing. *Materials Science and Engineering A*, Volume 530, pp. 87–97

Surapa, M.K., 2003. Aluminium Matrix Composites: Challenges and Opportunities. *Sadhana*, Volume 28, Parts 1 & 2, pp. 319–334

Toshiyuki, H.K., Michiaki, S., Seigi, A., 2006. Development of Aluminum Alloy Conductor with High Electrical Conductivity and Controlled Tensile Strength and Elongation. *Hitachi Cable Review No 25*

Weber, L., Dorn, J., Mortensen, A., 2003. On the Electrical Conductivity of Metal Matrix Composites Containing High Volume Fractions of Non-conducting Inclusions. *Acta Materialia*, Volume 51, pp. 3199–3211

Yi, W.Y., Lin, G., 2007. Effect of Particle Size on the Thermal Expansion Behavior of SiCp/Al Composites. *J Mater Sci*, Volume 42, pp. 6433–6438

Zhou X, Zou A, Hua X., 2009. Influence of Mg and Si in the Aluminum on the Thermo-physical Properties of Pressureless Infiltrated SiCP/Al Composites. *Mats. Sci. Forum*, Volume 610-613, pp. 546–553