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EFFECTS OF Al_2O_3 NANOPARTICLES ADDITION ON HARDNESS AND THERMAL PROPERTIES OF Al-Zr-Ce/Al_2O_3 WITH 3 wt% Mg NANOCOMPOSITE PRODUCED BY STIR CASTING

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ABSTRACT

EFFECTS OF Al_2O_3 NANOPARTICLES ADDITION ON HARDNESS AND THERMAL PROPERTIES OF Al-Zr-Ce/Al_2O_3 WITH 3 Wt-% Mg NANOCOMPOSITE PRODUCED BY STIR CASTING. Al-Zr-Ce alloy reinforced with Al_2O_3 nanoparticles with 3wt% Mg addition is proposed as one of the alternative material to replace ACSR as aluminum conductor. The composition of the nanocomposite consists of 0.12% Zr, 0.15% Ce, 3% Mg and 0.5-1.5 vf-% Al_2O_3. Fabrication of the nanocomposite is using stir casting method. Master alloy which consists of aluminum alloyed with Zr and Ce was manufactured. The master alloy was then melted and 3% Mg along with the reinforcement was blended inside the molten metal by stirring with rotational speed of 500 rpm at 850^{o}C in an inert Ar gas environment. Chemical composition test confirmed the composition of alloying elements were close to the design except Ce, that could be related to limitation of OES and fading effect. The density of nanocomposite was decreased, while the porosity was increased with the addition of Al_2O_3. Nanocomposites' hardness testing shows hardness increases with further addition of Al_2O_3, except the composite with 1.5 vf% of reinforcement that had lower hardness. Further addition of Al_2O_3 reinforcement to nanocomposite reduced its thermal expansion coefficient. SEM observation indicated that the Al_2O_3 nanoparticles were agglomerated and did not react to form interface layer. Nanocomposite 1.2 vf-% SEM observation shows that Ce inside of the microstructure did not segregate with Fe and Si, but seemed to react with Mg and Zr.

Keywords: Aluminum, Thermal, Hardness, Nanoparticles, Composite

ABSTRACT

EFEK PENAMBAHAN NANOPARTIKEL AL_2O_3 PADA KEKERASAN DAN SIFAT TERMAL DARI NANOKOMPOSIT Al-Zr-Ce/Al_2O_3 DENGAN 3 %BERAT Mg DIHASILKAN DENGAN PENGECORAN ADUK. Paduan Al-Zr-Ce diperkuat dengan nanopartikel Al_2O_3 dengan penambahan 3%berat Mg diajukan sebagai material alternative pengganti ACSR sebagai konduktor aluminium. Komposisi nanokomposit tersebut terdiri dari 0.12% Zr, 0.15% Ce, 3% Mg and 0.5-1.5 vf.% Al_2O_3. Fabrikasi material menggunakan metode pengecoran aduk. Paduan utama yang terdiri dari aluminium dipadukan dengan Zr dan Ce berhasil diproduksi. Paduan tersebut kemudian dilelehkan dan dicampurkan dengan 3% Mg bersama penguat dengan pengadukan berkecepatan 500 rpm pada temperatur 850^{o}C dalam lingkungan gas inert Ar. Pengujian komposisi kimia mengomfirmasi bahwa komposisi paduan hasil pengecoran mendekati dengan rancangan kecuali kandungan Ce, yang berhubungan dengan keterbatasan alat OES serta efek pengaburan kandungan. Densitas nanokomposit ditemukan berkurang, dengan kandungan porositas meningkat dengan peningkatan kandungan Al_2O_3. Kekerasan nanokomposit menunjukkan bahwa kekerasan bertambah dengan penambahan Al_2O_3, kecuali pada komposit dengan kandungan penguat 1.5 vf.% yang memiliki tingkat kekerasan lebih rendah. Penambahan penguat dapat mengurangi koefisien ekspansi termal komposit. Hasil pengamatan SEM dari nanokomposit dengan kadar penguat 1.2 vf% menunjukkan bahwa struktur mikro tidak bersegregasi dengan Fe dan Si, namun sepertinya bereaksi dengan Mg dan Zr.

Keywords: Aluminium , Termal, Kekerasan, Nanopartikel, Komposit

INTRODUCTION

The development of aluminum these days is advancing, with many efforts to improve not only its mechanical properties but also its thermal properties in order to satisfy the requirements for certain applications. One of the popular ways to achieve them is by making aluminum nanocomposite which involves alloying with several elements and reinforcing with nano-sized ceramics particles. Aluminum alloyed with Zr (zirconium) and Ce (cerium) and reinforced with Al_2O_3 is predicted to possess low weight and high electrical conductivity is proposed as material to replace the heavier and lower conductivity Aluminum Conductor Steel Reinforced (ACSR) which composed of steel wire in the core and aluminum wire surrounding it. ACSR is deemed to have high electrical resistance, causing it to produce more heat dissipation and thus, inefficient current transport.Wuhua Yuan *et al* reported that 0.145% addition of Zr in Al-Mg-Si cause slow reduction in hardness after heat exposure of 180°C for 400 hours that is attributed to the formation of Al_3Zr particle that could hinder recrystallization of Al [1]. Addition of Zr should be in small amount in order to preserve the electrical conductivity of the aluminum conductor. Cerium addition as reported by Chen *et al* is possible to not only boost mechanical properties of aluminum but also its electrical conductivity that would be suitable as a conductor material [2]. The conductivity of aluminum also depends on elements dissolved in it, including alloying and impurities.

The addition of Al_2O_3 nanoparticles into aluminum, is expected to further increase its mechanical properties such as tensile strength, hardness, etc. and also its thermal resistance properties, such as thermal expansion. Previous investigation by K.Milos *et al* showed that the addition of micron size Al_2O_3 with content ranging from 20-50 wt-% into the Al matrix significantly decrease the CTE (Coefficient of Thermal Expansion) value [3]. Since the restriction effect of reinforcing particles causes CTE reduction, it is expected that by using nanoparticles as reinforcements would even further reduce composite CTE. Moreover, the addition of Mg as wetting agent to form spinel ($MgAl_2O_4$) with the reinforcement and matrix theoretically gives better thermal resistance because of better bonding between them.

The purpose of this paper is to investigate the effect of Al_2O_3 nanoparticles addition on Al-0.12%Zr-0.15%Ce with the addition of 3-wt% Mg on the hardness and thermal expansion properties. The results are expected to provide useful information in the fabrication procces when making an all aluminum conductor.

EXPERIMENTAL METHOD

Master alloy Al-Zr-Ce 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 the temperature ranging from 750-800°C and then decreased to 700°C. At this temperature, Al-Zr and Al-Ce alloy was introduced into the melt and then stirred to distribute all of the alloying elements evenly. It was then poured into 800 gram ingot mould.

Al-Zr-Ce/Al_2O_3 nanocomposite with addition of 3-wt % Mg was made through stir casting method. Al_2O_3 content was varied from 0.5, 0.7, 1.0, 1.2 to 1.5 % volume fraction (vf) of composites. Prior to composite fabrication, Al_2O_3 particles with the size of 80 nm supplied by US Nanomaterials Research, Inc. were deagglomerated by crushing, using mortar and stamper along with 3-wt% stearic acid as process control agent (PCA) and baked at 400°C for 2 hours. After that, Al-Zr-Ce master alloy was lined up in crucible and heated to 850°C for 2 hours. Pure magnesium, supplied by PT Baralogam Multijaya, was added after dross on the surface was removed, stirred and degassed using Ar for about 1 minute. Al_2O_3 particles was then added into the melt, stirred and degassed at the same time with rotational speed of 500 rpm for about 3 minutes. After stirring was done, the melt was poured into plate mold.

Produced samples were characterized with several testings. Density measurement of the samples was evaluated based on Archimedes method, using A&D GF3000 Digital Scale. Brinell Hardness Test was conducted to measure the hardness of the nanocomposites using indenter with the diameter of 2.5 mm at a load of 31.25 kg. The hardness value was averaged from five indentation readings. Thermal expansion testing was performed by using push-rod dilatometer at Center for Physics Research, LIPI. The size of the sample used for this measurement was 5-5.5 cm length and 0.5 mm diameter. The variables, which is the content of Al_2O_3 particles in the Al, was measured using three samples each and tested at the temperature range of 150-350°C. The samples were placed into a holder, between push-rods. When heat was applied, the expansion of the samples was measured by the push-rod equipped with a sensor, relative to the time. Microstructural observation was conducted using Inspect F50 FE-SEM to reveal the presence of reinforcement and give elemental observation on each components of the microstructure. Each samples were prepared with metallographic preparation using SiC paper, TiO_2 polishing particles and Keller's reagent etching for 15-30 s. FE-SEM observation was also employed to measure the deagglomerated Al_2O_3 nanoparticles in order to analyze the size and shape of the reinforcement.

RESULTS AND DISCUSSION

Chemical Composition Analysis

Chemical composition of the fabricated nanocomposite is as presented in Table 1. The elements like Zr and Mg were already in the range of the targeted composition, while Ce seems to be outside it. The reason behind this perhaps was caused by limitation of OES instrument to detect Ce inside of the material and fading effect of Ce that could turn Ce into oxides and reduced its content in the material during the melting of master alloy [4]. Fe and Si had also been found in quite high percentage too that could be caused by the contamination coming from the stirrer and other dust around the crucible.

Table 1. Chemical composition of master alloy and nanocomposites

Sample	Elements (wt-%)					
	Zr	Ce	Mg	Si	Fe	Al
Master alloy	0.1080	0.0020	-	0.3800	0.7360	Bal.
0.5% Al_2O_3	0.1140	0.0055	3.3800	0.3870	0.8080	Bal.
0.7% Al_2O_3	0.1200	0.0058	2.9300	0.4410	1.1100	Bal.
1.0%Al_2O_3	0.1090	0.0055	3.4600	0.4350	1.0700	Bal.
1.2%Al_2O_3	0.1050	0.0065	3.4500	0.4480	0.8960	Bal.
1.5%Al_2O_3	0.1200	0.0063	3.0500	0.3900	0.7970	Bal.

Density and Hardness Properties Analysis

Density and porosity test result using Archimedes method is shown in Figure 1(a). Theoritical and actual density of nanocomposite formed certain trends, where the former has incremental trend and the latter has decremental trend. The decremental trend of actual density was caused by hydrogen gas that might be absorbed during fabrication, forming pores in the nanocomposite. With more addition of reinforcement which has low wettability, more pores would form, especially around the nanoparticles. The hypothesis is confirmed with % porosity of nanocomposite, although it appeared to be lower than other investigator who study the same particles with relatively same size [5].

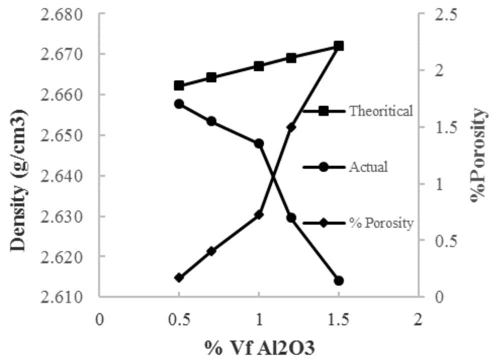

Figure 1. Effect of Al_2O_3 content on density and porosity

Hardness testing result can be seen in Figure 2. The trend formed that is influenced by the content of Al_2O_3 nanoparticles is seemed to be incremental up to 1.2-vf%. The result found in this experiment was higher than similar nanocomposite (Al-Zr-Ce/$Al_2O_{3(np)}$) but without addition of Mg that was investigated by Kirman *et al* [6]. The role of nanoparticles inside of aluminum matrix is mainly to act as a barrier to impede the dislocation movement. Other roles of nanoparticles inside of the matrix is to better load-distribution, acting as grain refiner and also producing stress that comes from CTE mismatch between the particles and matrix [7]. The more the content of reinforcement particles in the matrix, the higher the strength of the material, including hardness value. The presence of Mg inside of the nanocomposite helps to improve the bonding of reinforcement and matrix by forming $MgAl_2O_4$.

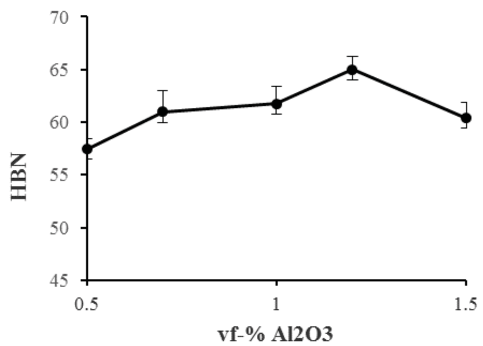

Figure 2. Effect of Al_2O_3 content on hardness.

The hire concentration of reinforcement to give highest hardness number is 1.2% with 65 HBN. Further addition of Al_2O_3 at 1.5 vf-% reduced the hardness value of materials. Several investigations also points out this same trend of result, even though the peak concentration of reinforcements where it reached maximum hardness value. Study by Sekar *et al* shows that the peak concentration of nano-sized Al_2O_3 in A356 produced using combination of stir casting and squeeze casting is 1.0%, which reach about 70 HRB or 128 HBN, whereas report by Ezatpour *et al* finds the same peak concentration of reinforcement but with hardness value of around 70 HBN in Al 6061/Al_2O_3 nanocomposite produced by stir casting [8-9]. Both of the investigations did not include 1.2% of reinforcement.

The reason behind difference in result but related trend might come from the combination of factors that build composite strength, such as porosity distribution, nanoparticles distribution and agglomeration, bonding between matrix and particles [9]. Mainly, agglomeration of nanoparticles which is often found in any nanocomposites, causing several effects that could reduce its hardness, such as uneven load-transfer with the matrix and ineffective grain refiner compared to nanoparticles. In order to reduce agglomeration, further study needs to be done with other mechanical milling variables, such as longer milling time and also better casting condition.

Thermal Expansion Analysis

Thermal expansion of the nanocomposite was measured using dilatometer at temperature range of 150-350^{o}C. The result is shown in Figure 3. It is observe that nanocomposite yields lower CTE value than unreinforced alloy, and with increasing nanoparticles content inside of the nanocomposite could further reduce its CTE value. This result was caused by the restricting effect of nanoparticles to the matrix. When heat was applied to the nanocomposite, matrix that has bigger CTE value than reinforcement would tend to expand. The reinforcement would then hold the matrix from expanding. The smaller the particle, the smaller CTE value that could be achieved by the nanocomposite. The reason behind this is that smaller particles tend to have more number of particles with interfacial reaction than the larger ones [10]. CTE difference between the unreinforced alloy with nanocomposite was not significant, despite of the decrement. This could be attributed with uneven distribution of reinforcing particles, because it is one of the weaknesses of stir casting that leads to the agglomeration of the reinforcing particles. Agglomerated particles could also produce higher CTE value. Better distribution and deagglomeration of the nanoparticles would boost its thermal resistance even further.

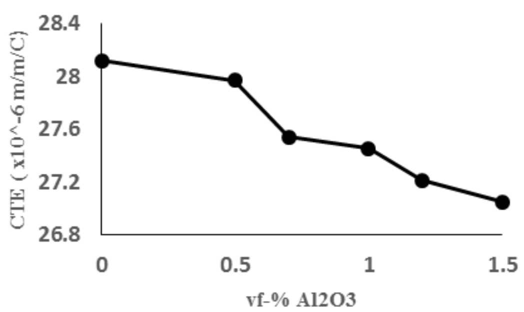

Figure 3. Effect of Al_2O_3 on coefficient of thermal expansion (CTE) of Al-Zr-Ce/Al_2O_3 nanocomposite.

Particles and Microstructural Analysis

Analysis of the nano particles using SEM is shown in Figure 4. The size of the particles were larger than initially designated. Since the particles were kept inside of the storage the chances for them to agglomerate with each other were high, nanoparticles's surface energy are high. Further preparation using mortar and PCA did not give good size reduction to the particles, even though 3 wt-% stearic acid is believed to reduce Al_2O_3 particles before cold welding happens, while lower amount of it was found to produce agglomeration [11]. Better deagglomeration process using ball mill with longer milling time is suggested to be done next in order to achieve finer size of Al_2O_3 nanoparticles.

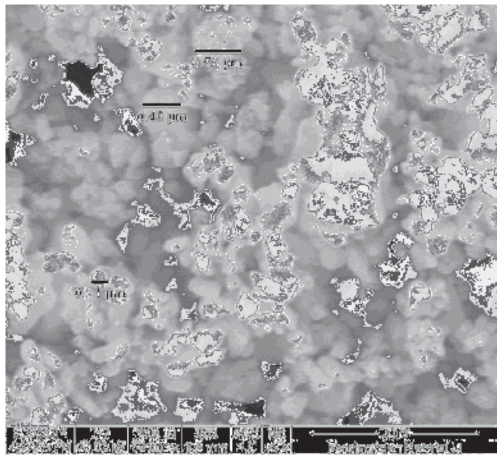

Figure 4. The prepared Al_2O_3 nano particles using mortar and PCA.

SEM observation is shown in Figure 5 with EDS analysis in Table 2. Al_2O_3 was found unreacted with Mg in what appears to be a pore in Al-Zr-Ce/1.0vf-% Al_2O_3 (spot 1) eventhough the area surrounding it has already reacted, judging from the amount of Mg (spot 2) as seen in Figure 5(a). This unreacted particle seemed to be caused by the low speed of reaction of Mg to form $MgAl_2O_4$. It was investigated by McLeod *et al* that the higher the process (melting) temperature during fabrication led to deceleration of $MgAl_2O_4$ reaction rate with high melting temperature [12]. The size of the particle was even bigger compared to the prepared powder. This perhaps was caused by two things, which are the stirring

Table 2. EDS spectrum in figure 4

Spot	Composition [wt-%]						
	O	Mg	Al	Si	Zr	Ce	Fe
1	37.66	0.37	61.97	-	-	-	-
2	5.46	3.32	91.21	-	-	-	-
3	1.14	5.58	75.12	0.20	1.83	15.83	0.30
4	1.78	2.95	87.29	0.33	1.79	0.35	5.50
5	5.43	3.49	78.74	10.10	1.67	0.29	0.28
6	6.10	3.66	77.62	10.40	1.33	0.56	0.33
7	0.81	2.38	93.78	0.16	1.82	0.69	0.36

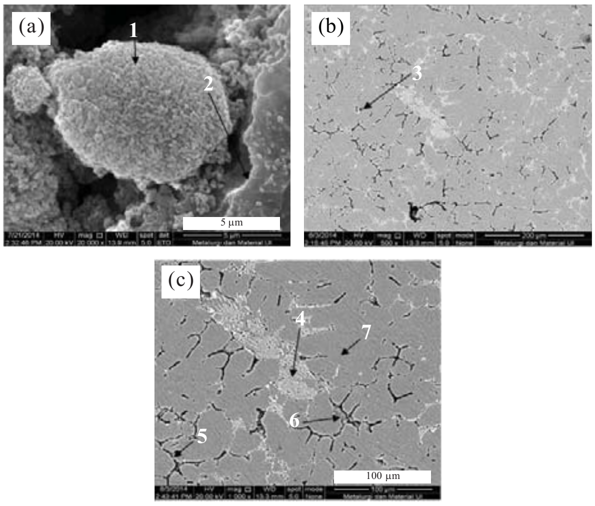

Figure 5. Microstructure of nanocomposite. (a) agglomeration found on a pit in Al-Zr-Ce/1.0 vf-% Al_2O_3, x20,000, (b) Microstructure of Al-Zr-Ce/1.2vf-% Al_2O_3, x500, (c) more detailed observation of Al-Zr-Ce/1.2 vf-% Al_2O_3, x1000

motion of the melt after introduction of reinforcement causing coalescence between them and the slow reaction with Mg causing chance of the particles to agglomerate again were high.

Figure 5 (b) shows microstructural observation of Al-Zr-Ce/ 1.2 vf-% Al_2O_3. The microstructure shows distinctive shapes of intermetallic compounds and also pores. The EDS spectrum in spot 3 gives high percentage of Ce elements along with Mg and Zr. Ce role in the material is to segregate with the impurities (Zr, Mg) to form intermetallic compounds so that the electrical conductivity could be improved. Electrical conductivity in aluminum depends on how well electron is transported in it. One of the factors that plays a crucial role is the content of other solute elements. The elements has potential to scatter in aluminum, hence the electrical conductivity is decreased. Unfortunately, other impurities such as Si and Fe content that segregated along with Ce in the spot appears to be of small percentage.

At a bigger magnification as shown in Figure 5(c), spot 4 points a noticeable percentage of Fe that clearly an intermetallic compound of Al and Si, eventhough Si seemed to be in small percentage. This compound could be Al_3Fe intermetallic. In spot 5 and 6, Si percentage is high, along with O and Mg. The compound is possibly Mg_2Si intermetallic compound, along with Al_2O_3 there. In spot 7 in what appears to be the matrix of the nanocomposite, Zr content in form of solid solution, Al_3Zr intermetallic compound appears to be high. There is also noticeable content of Ce. This means that the presence of other impure elements that can distract the movement of electron in the matrix, halting the electron transport and finally reducing the overall electrical conductivity of the nanocomposite[2]. Fe content is in small amount, which could be caused by the tendency of the element to form intermetallic with other elements.

CONCLUSION

Al-Zr-Ce reinforced with Al_2O_3 nanoparticles and with addition of 3 wt-% Mg composite was successfully produced using stir casting method, but Ce content could not be confirmed because of its possible fading effect. Density decreases and porosity increases with addition of Al_2O_3. The hardness was found increasing with addition of Al_2O_3 up to 1.2 vf-%, since the nanoparticles acted as dislocations barrier along with several other strengthening mechanism. The addition of 1.5 vf-% Al_2O_3 decreased hardness value, caused by combined effects of uneven distribution, high amount of porosity, and agglomeration of reinforcement. Thermal expansion in 150-350°C nanocomposite decreases with further addition of Al_2O_3 because Al_2O_3 could halt the expansion of Al-Zr-Ce matrix during the exposure of heat, but the effect was still insignificant since the reinforcement was agglomerated. The preparation of reinforcing particles using mortar and PCA was not effective to reduce the size of Al_2O_3 nanoparticles. This resulted in agglomerated particles in large size which can be found in the fabricated nanocomposite, which appeares to be unreacted with Mg to form spinel since the deceleration rate of reaction of the compound. Intermetallic compounds that could be found inside of the composite was due to the excessive amount of impurities, Ce intermetallic did not effectively segregate with Fe and Si, but still could segregate well with Mg and Zr.

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