THE EFFECT OF Mg-Al Wt% FOR PHASE FORMATION OF SPINEL $MgAl_2O_4$ PRODUCED BY METAL DISSOLVED METHOD

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ABSTRACT

Synthesis of magnesium aluminate spinel powder ($MgAl_2O_4$, abbreviated as MA) were prepared by the liquid mixing method. The synthesis of MA involved Mg powders with various weight compositions (4.8; 10; 20; 30; 40; and 60%) and Al powders (95.2; 90; 80; 70; 60 and 40%) as the raw materials, which were independently dissolved in 37% HCl to form $MgCl_2$ and $AlCl_3$ solutions. Both solutions were then mixed and stirred for 5 hours and dried to a temperature of about 100-105°C to produce powders with different weight compositions. Each powder resulted from drying was characterized using DTA-TGA, and then calcined at 650 °C; 750 °C and 850 °C for 1 hour. The calcined powder was characterized by XRD to qualitative and quantitative analyses using Rietica. It was found that MA samples contained only $MgAl_2O_4$ and MgO as the impurity phase. The relative weight fraction of $MgAl_2O_4$ increased up to 99% for 95.2 wt% Al. Using an extrapolative approach to determine the Mg-to-Al composition, nearly pure MA, as high as 99%, was achieved at 95.2% Al and 4.8% Mg.

Keywords: Metal dissolved Method; $MgAl_2O_4$; Weight Fraction.

Introduction

The development of nanomaterial technology indirectly influences on of nanocrystalline ceramic materials. Nanocrystalline material is expected to improve the properties of the material, especially in physical, mechanical, optical, and others. Magnesium Aluminate spinel (MA) is a well-known ceramics material with good mechanical strength, thermal, chemical and optical. MA has been widely used in various applications and as a refractory material because it has a high melting temperature (2135 °C). It is, therefore, a good candidate material for high-temperature applications.[1]

MA is a ceramic with a cub[1] ic spinel structure which is based on the oxygen sublattice FCC closed-packed place where the tetrahedral and octahedral sites are filled. In general, the structure of spinel written as AB_2O_4 with A as a divalent cation and B is a trivalent cation. Spinel has two types namely normal and inverted. For normal spinel, like MA, B^{3+} cations occupied 1/4 the positions of octahedral and A^{2+} cations occupied 1/8 of the tetrahedral positions. There are several methods for synthesizing magnesium aluminate such as hydrothermal,[2] microwave-assisted combustions,[3] Thermal Plasma,[4] and sol-gel.[5] Microwave-assisted combustion method, however, needs a long processing time to acquire pure MA, and the Thermal plasma spray and hydrothermal techniques are expensive and resulted in MA with MgO and Al_2O_3 impurities. In addition to those, the sol-gel method is also relatively costly. Moreover, these synthesis methods do not have sufficient control on phase formation of MA too.

Analyses of the formation of the MA phase in a MgO-Al_2O_3 ceramic composite system

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were also reported by researchers. It was found that MA abundant will increase with more weight percentage of MgO and reached a maximum value in an equimolar Al_2O_3-MgO system.[6] Studies on the synthesis of pure MA are developing, i.e. in finding the most effective synthesis method by studying the formation of MA. Recently, a relatively simple synthesis method, called the metal-dissolved method was introduced. The method consists of mixing of solutions of metal precursors, drying at a temperature of 100-105 ºC and finally calcination at a given temperature to obtain an oxide compound of the constituting elements. This method offers an alternative to producing nanoparticles by a bottom-up approach.[7]

In this study MA, spinel powders were synthesized using the metal-dissolved method with Mg–to-Al weight ratio variations to study the formation of spinel.

Methods

Synthesis of MA spinel has been done from Mg and Al powders. Mg and Al powders as the precursors were prepared at various weights composition (4.8; 10; 20; 30; 40 and 60% by weight) - Al (95.2; 90; 80; 70; 60 and 40% by weight). Synthesis begins by dissolving magnesium powder (Merck) without heating in a 37% HCl and stirred with a magnetic stirrer for 1.5 hours at a constant speed. Then the synthesis was continued by dissolving aluminium powder (Merck) without heating in a 37% HCl and stirred with a magnetic stirrer for 3 hours at a constant speed. All metals ($MgCl_2$ and $AlCl_3$ solutions) are mixed and stirred for 5 hours at a constant speed. Then the solution mixture is dried at 100-105 °C to produce powders with different weight compositions. Each of the dried powder was calcined at 650, 750 and 850 °C for 1 hour. following DSC-TGA results, X-ray diffraction (XRD) was used for phase characterization, including phase composition analysis using *Rietica*,[8] using the 'ZMV' relative method to determine relative weight fraction of each phase:

$$W_i = \frac{s_i(ZMV)_i}{\sum_{k=1}^{n} s_k(ZMV)_k} \quad (1)$$

where W_i is the relative weight fraction of phase *i* (%), *s* is Rietveld scale factor, *Z* is the number of chemical formulas in the "a" cell, *M* is the mass of the phase and *V* is the volume of the unit cell.

Table 1. Nomenclature sample in this study

Temperature	Mg-Al (wt%); MA = Magnesium Aluminate					
	4,8-95,2	**10-90**	**20-80**	**30-70**	**40-60**	**60-40**
650°C	MA4965	MA1965	MA2865	MA3765	MA4665	MA6465
750°C	MA4975	MA1975	MA2875	MA3775	MA4675	MA6475
850°C	MA4985	MA1985	MA2885	MA3785	MA4685	MA6485

Result and Discussion

Fig. 1 show the representative DSC-TGA curve for the 40% Mg and 60% Al (MA46) sample taken a heat rate of 10 °C/min up to 1000 °C. The initial sample weight was 20.2 mg. DSC result from the dried MA spinel powder indicated phase transformation at certain temperatures. There are four sharp endothermic peaks at 173, 205, 274 and 479 °C. The peak at 173 °C is addressed to the evaporation of water which is followed by a drastic absolute mass reduction, i.e. up to 1.6013 mg. The peak at temperature 205 °C can be associated with a phase transformation from Al to Al_2O_3 which is accompanied by a mass reduction of 1.8472 mg while that at 273.78°C can be associated with MgO phase transformation. The thermal events above 300 °C are all exothermic which possibly due to the phase formation of MA spinel as a result

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of the reaction between previously formed Al_2O_3 and MgO.[9] The MA formation completes above 478.68 °C, with its crystallinity, should be further observed. Since in principle, there is no reaction or decomposition from 557 °C to 1000 °C. as marked by steady TGA curves, the calcination temperature was focused on 750 °C. The previous researchers[10] with the Sol-gel method showed that at temperatures 500-700ºC the spinel had begun to form but was still amorphous with larger crystal size and the crystal spinel phase would begin to form at a temperature of 800ºC. Therefore, this study used calcination temperature in the range of 650-850 °C.

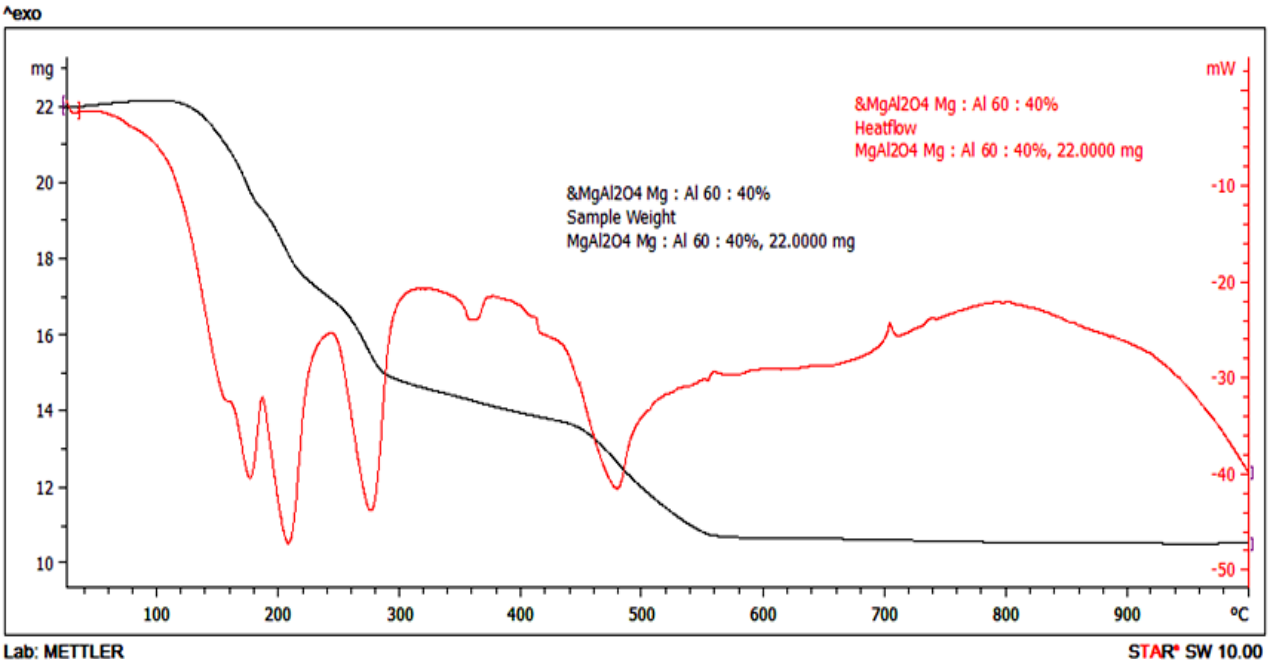

Figure 1. DSC-TGA curve of MA46 (40%:60%) dried sample. The heat rate was 10 °C/min.

Figure 2-4. shows the X-ray diffraction patterns of MA samples at calcination temperature variations with a holding time of 1 hour. These patterns indicate that the phases identified were only spinel (MA) ($MgAl_2O_4$ with PDF no. 21-1152) as the main phase of spinel and periclase (MgO with PDF no.45-0946) as impurity phase in the absence of the aluminium oxide phase which is identified. The spinel formation as shown in the pictures shows that the method of the metal dissolved method with HCl solvent can be used for the synthesis of spinel MA. From the diffraction patterns presented in Figure 2-4, it can generally inform that synthesis of spinel MA on all temperatures, the relative intensity of periclase to spinel decreases with increasing Al composition. This decrease occurred very sharply, which is about four times the composition of Al: Mg = 40: 60 to almost zero in the composition of 95: 4.

From the diffraction patterns in Figure 2-4. it can also be observed that diffraction patterns have slightly different peak widths. If it is assumed that a bottom-up synthesis method such as metal dissolved method has no residual strain effect on the product material, then the widely of this peak can be assumed to be related only to the size of the crystal. In general, MA intensity is relatively higher than the intensity of periclase, and also MA intensity increases with the increase of Al content. All patterns do not show an Al_2O_3-related peak, indicating that the Al precursor has completely reacted with the Mg precursor to form MA spinel. It is believed that MA is formed from a reaction between the oxidized dissolved magnesium and aluminium. Thus, the difference in width of the peak indicates

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that the size of the crystals in the phases in the samples has a significant difference. Specifically for the MA spinel phase, a fairly large peak widely indicates that the phase is on the nanometer crystal size.

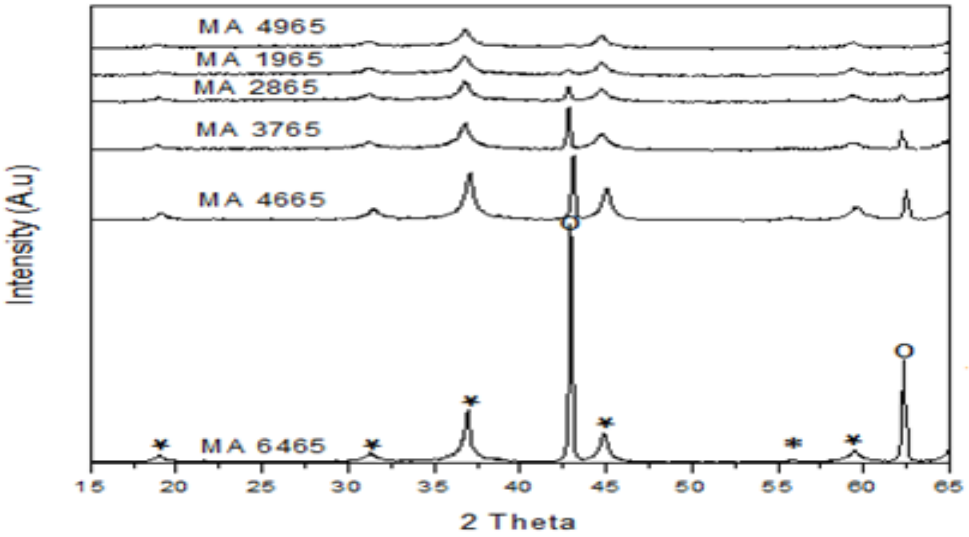

Figure 2. XRD patterns (λ=1.54060 Å) for MA samples with various composition calcined at 650 °C.: ∗ = MA, o = Periklas.

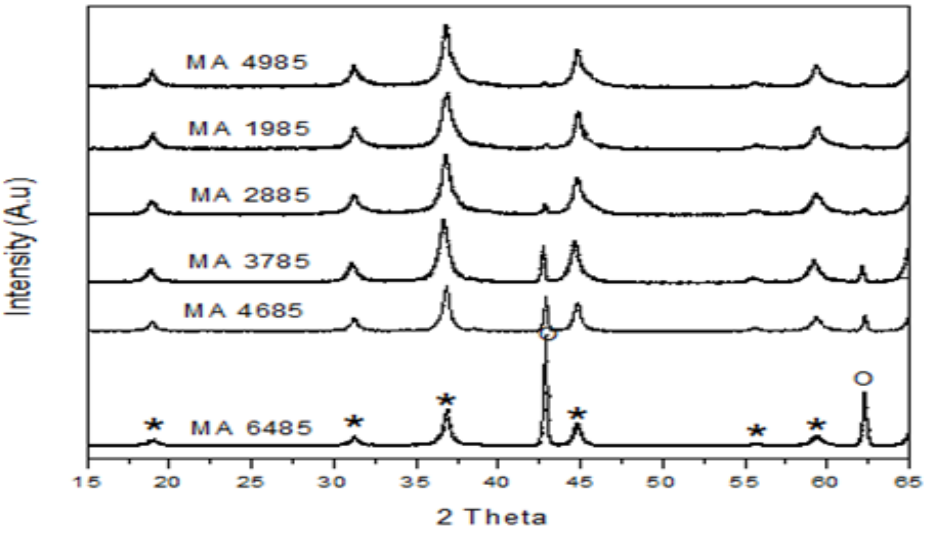

Figure 3. XRD patterns (λ=1.54060 Å) for MA samples with various composition calcined at 850 °C.: ∗ = MA, o = Periklas.

Table 2. presents the Rietveld refinement figures-of-merit (FoM) values for samples with different compositions. Refinement for all samples is acceptable because the value of the GoF (goodness-of-fit) is less than 4%. These refinement results are explained about weight fraction to show composition weight fraction of MA and periclase. its also supported by the minute difference plot between the calculated and observed pattern as shown in Fig. 5. Then, the refinement outputs can be used for further analyses.[8]

Fig. 6-8 presents the relative weight fraction of each identified phase in the samples, calculated using formula (1) which has been embedded in Rietica software. Clearly the MA and periclase (MgO) weight fractions change complementary as the Mg-to-Al content changes. The more Al the less MA. In other words, within the vicinity of the

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composition, more Mg is required to form pure MA. The highest MA content is reached at 90:10 Mg-to-Al composition, attaining a value of as high as 98%. This result implies that a certain Mg-to-Al composition can be calculated, obviously by extrapolation, to achieve pure MA. Such extrapolated Mg-to-Al composition was 95.2:4.8%, which should then be used to prepare a new sample with expectedly pure MA.

Table 2. FoMs values from the Rietveld refinements (using *Rietica*) of XRD patterns.

Sample	Figures-Of-Merit			
	R_p(%)	R_{wp}(%)	R_{exp}(%)	GoF
MA4965	9,0	11,3	9,2	1,4
MA1965	9,0	11,3	9,3	1,4
MA2865	9,4	12,1	9,0	1,7
MA3765	9,2	11,4	9,1	1,4
MA4665	11,5	14,3	9,1	1,9
MA6465	12,6	13,1	9,0	1,8
MA4975	9,6	12,2	9,8	2,0
MA1975	9,8	12,1	9,8	1,7
MA2875	9,5	12,1	8,3	1,9
MA3775	8,6	11,2	8,6	1,6
MA4675	8,6	11,1	8,3	1,7
MA6475	9,6	12,3	9,6	1,6
MA4885	12,9	18,6	9,8	1,9
MA1985	12,5	16,9	10,9	1,6
MA2885	13,0	16,4	9,4	2,2
MA3785	13,9	18,2	9,8	2,1
MA4685	12,4	15,8	9,8	2,1
MA6485	12,3	18,8	10,2	2,0

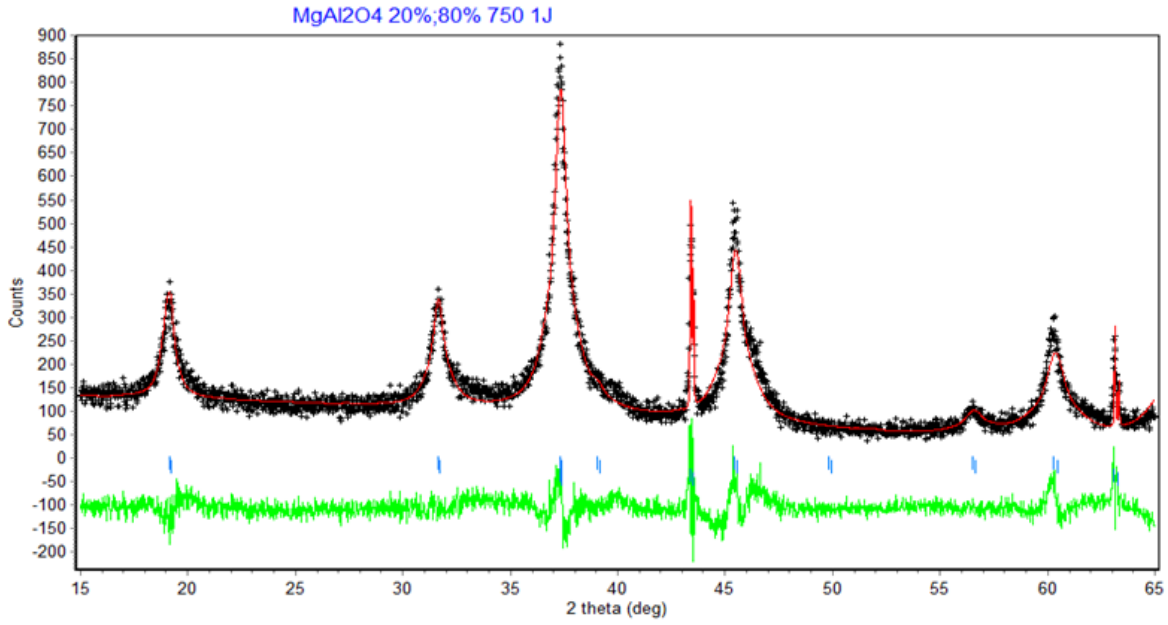

Figure 4. Typical Rietveld refinement plot using Rietica from the MA2080 sample. The observed pattern is described by (+++) symbol while the calculated pattern by a red straight line. The bottom green curve is a plot of the difference between the measured and calculated patterns. Small vertical straight lines represent diffraction peak positions.

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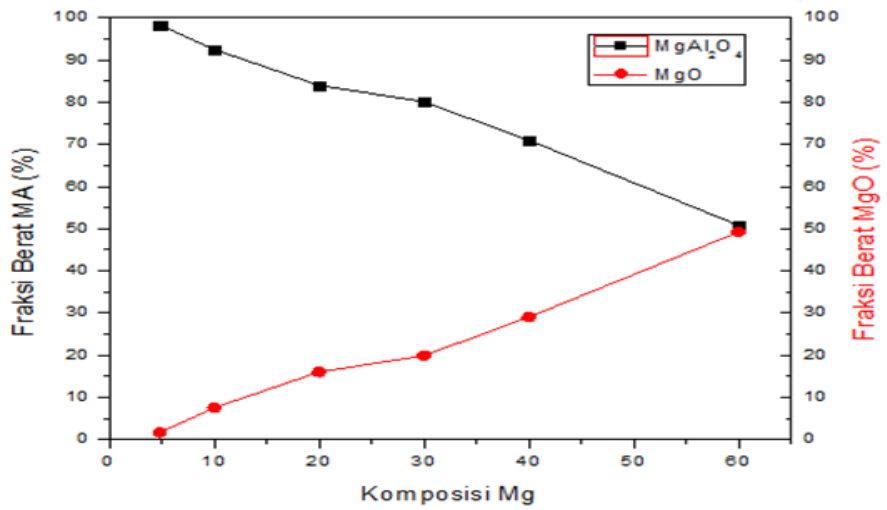

Figure 5. The relative weight fraction of MA phases samples for various Mg-to-Al compositions at 650 °C.

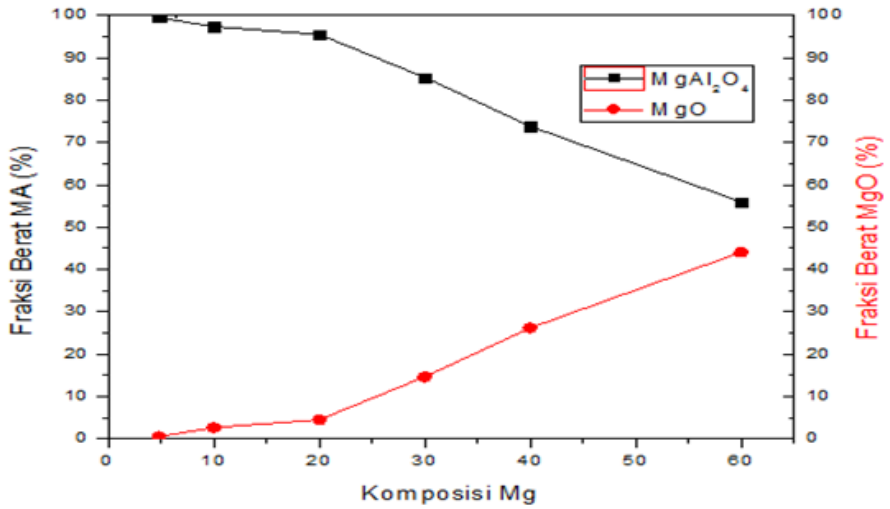

Figure 6. The relative weight fraction of MA phases samples for various Mg-to-Al compositions at 750 °C.

Periclase (MgO) phase is formed because most of Mg does not react completely with Al. Theoretically, if the Al^{3+} ions replacing Mg^{2+} ions, the cation vacancy defects (Mg) can be generated. Cation vacancy defects can accelerate the process of cation diffusion which improves densification and grain growth accelerates later.[11] The process of Mg^{2+} ions replacing Al^{3+} ions is accompanied by the formation of oxygen vacancies. Theoretically, this flaw does not affect the diffusion of cations which control grain growth. More Al^{3+} cation diffusion will further accelerate the oxidation reaction of metallic Mg and Al. Excess Al composition will facilitate the formation of a more homogeneous solution to form MA. Part of the MA formed was probably amorphous, which will diminish by synthesis at a higher temperature (above 1000°C).

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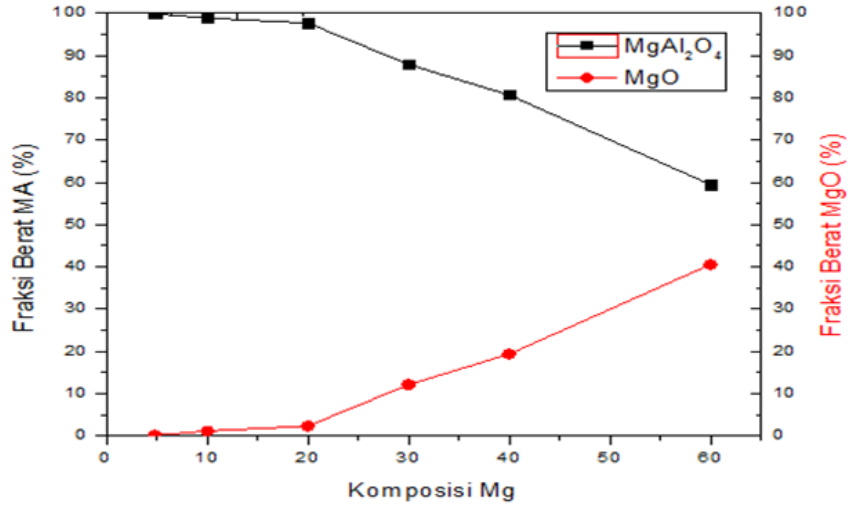

Figure 7. The relative weight fraction of MA phases samples for various Mg-to-Al compositions at 850 °C.

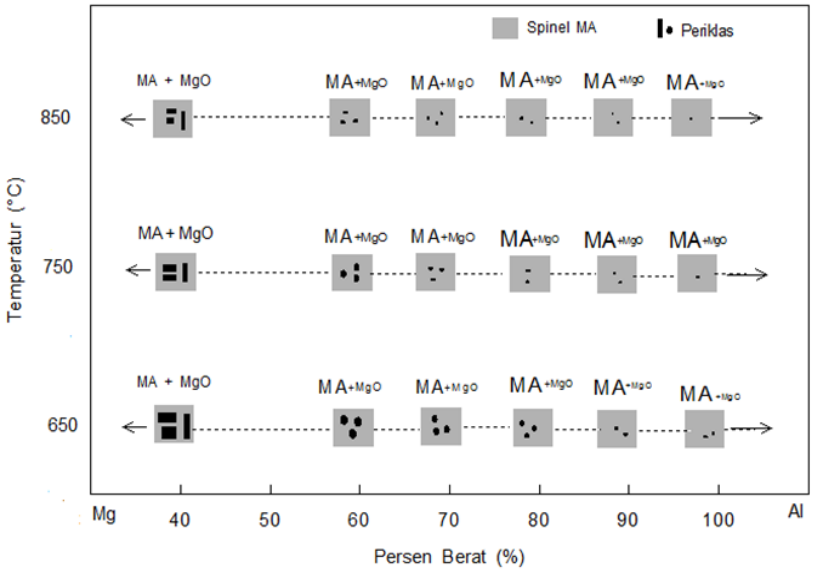

Figure 8. Phase Diagram of Mg-Al System for Spinel Formation

The primary phase of spinel is formed due to the reaction between magnesium and aluminium oxidized dissolved. this is suitable for reaction (2) below.

$$MgO + \alpha - Al_2O_3 \rightarrow MgAl_2O_4 \quad (2)$$

$$Al_2O_3 \rightleftarrows 2Al^{1+}{}_{(Mg)} + 3O_{(O)} + V^{2-}{}_{(Mg)} \quad (3)$$

where, Al^{1+} is Al ion which site of Mg sublattice, $O_{(O)}$ is oxygen ion which site of oxygen sublattice and V^{2-}(Mg) = defect of Mg and

$$2MgO \rightleftarrows 2Mg^{1-}{}_{(Al)} + 2O_{(O)} + Vo^{2+} \quad (4)$$

where Mg^{1-} is the Mg ion in the sublattice site of Al while $O_{(O)}$ is oxygen ion in the sublattice site of oxygen and Vo^{2+} is oxygen defect.

Figure 8 showed a phase diagram formed from variations composition of Mg-Al at each calcination temperature variation. Based on

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the MA spinel phase diagram the MgO-Al_2O_3 system with the solid-state reaction method. At temperatures between 650-850 ° C in the composition of 10-60% Al_2O_3 the formed phase is spinel and periclase, and for the composition of 70%, Al_2O_3 pure spinel is formed, whereas, for 80-90% Al_2O_3 composition, the formed phase is spinel and Al_2O_3.

The results of this study, using comparison of composition from the base material Mg-Al with the metal dissolved method was obtained that at the composition of 95.2, 90, 80, 70, 60 and 40% Al, the phases formed at each calcination temperature variation were the same that spinel as the main phase and periclas as impurity phase.

This phase diagram is confirmed by DSC-TGA data in Figures 1 which explains that at temperatures above 470 ° C the spinel phase has begun to form. The periclas phase that emerged in all samples was confirmed by the exothermic peak in Figure 1 in the temperature range 271-432 ° C. other research confirms that states at the temperature of 400-600 ° C, the periclas crystalline phase has been formed perfectly. The absence of a phase change marked by the absence of the Al_2O_3 phase is due to the fact that the alumina phase can crystallize perfectly at temperatures above 1000 ° C, so there is always an excessive periclase phase. Formulation (2) shows that the spinel phase is formed due to the reaction between magnesium and aluminium oxidized dissolved which is α-Al_2O_3phase. This is what causes the appearance of periclase in all samples because not all periclas crystals produced can react with alumina that has not fully crystallized at the calcination temperature used in this study.

Conclusion

It can be concluded from this study that MA spinel formation using the metal-dissolved method with five different Mg-to-Al metal powder compositions contained two phases, namely MA and periclase after calcination of the mixed precursors at 650 °C-850 °C for 1 hour. The MA-periclase composition depends on the Mg-to-Al composition and between the Mg-to-Al composition range observed, more MA was obtained with increasing Al. The maximum amount of MA was around 99% (by weight) at the 4.8:95.2 Mg-to-Al composition.

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