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Effect of Alumina addition on the Phase Composition of Cordierite Precursors from Rice Husk Silica

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Abstract

This study describes the phase composition change of cordierite ceramics by mixing Al_2O_3 and cordierite. The mixture was sintered at temperature of 1230 ^oC with different alumina content relative to cordierite. The phases formed and structure changes as a result of alumina addition were investigated using different characterisation technique of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Density, porosity, hardness and electrical resistivity were also measured. The results obtained revealed that addition of alumina caused the tranformation of cordierite phase into alumina, crystobalite, spinel and periclase phases. Density porosity and hardness increased with increasing alumina content, while electrical resistivity decreased with increasing alumina content.

Abstrak

Penelitian ini menggambarkan perubahan struktur/komposisi cordierite dengan mencampurkan Al_2O_3 and cordierite. Selanjutnya campuran disinter pada temperatur 1230 ^oC dengan konsentrasi alumina yang berbeda. Perubahan dan pembentukan struktur/fase yang terbentuk hasil penambahan alumina dikarakterisasi dengan Metode XRD dan SEM. Densitas, porositas, kekerasan dan resistivitas diukur. Hasil yang diperoleh menunjukkan bahwa cordierite mengalami transformasi menjadi alumina, crystobalite, spinel dan periclase dengan penambahan alumina. Densitas, porositas dan kekerasan meningkat dengan meningkatnya alumina, sementara restivitas listrik mengalami penurunan dengan meningkatnya alumina.

Keywords: Cordierite, rice husk, microstructure, structure

1. INTRODUCTION

Cordierite ($2MgO.2Al_2O_3.5SiO_2$) represents techically important ceramic which is applicable in a variety of areas. Due to its low dielectric constant (e= 5-6), high resistivity (r> 10^{12} Ω cm), high chemical durability, high resistance to thermal shock and very low thermal expansion coefficient (α = 1-2 x $10^{-6}/^oC$, cordierite ceramic is a promising candidate in many application. Some examples of the application are heat exchangers for gas turbine engines (Laokula and Maensirib, 2006), electrical and thermal insulation (Gonzalez-Velasco, *et.al*.,1999; Evans *et.al*., 1980), high integral circuits, microchips, (Janackovic, *et.al*., 1997), display panels (Sarkar, *et.al*., 2003), and multilayer chip indicators (Wang, and Zhou, 2004). In previous studies (Oliveira and Fernandez 2002; Lim and Jang 1993), have established that the excellent thermal shock resistant material when it is subjected to rapid changes in temperature. They found that fracture toughness increases with increasing sintering temperature from 1250 to 1300 ^oC.

There are many studies on the synthesis of cordierite using talc and kaolin as starting raw materias together with other minerals such as magnesium compounds, silica, alumina, gibsite, calcined alumina and fly ash mixtures (Banjuraizah, *et.al*., 2009; Saha, *et.al*., 2001), fumed silica, bauxite and talcum **(**Ewais, *et.al*., 2009), talcum, kaolin, fieldspar and sepiolite **(**Acimovic, *et.al*., 2003). Most of the compounds were made following the solid-state reaction route. The solid state-reaction route from these natural mineral usually also results in the presence of secondary phases together with cordierite such as spinel, cristobalite, mullite and forsterite. Beside solid state reaction, another method that has been studied extensively is sol-gel method. This method has been previously applied (Petrovič, *et.al*., 2003) to prepare cordierite by mixing raw materials of aluminum isopropoxide, magnesium ethoxide, and tetraethylorthosilicate in absolute ethanol, revealed that μ-cordierite crystallized at

temperature range of 950-1000 °C accompanied by the formation of spinel in small amount, and transformation of μ into α-cordierite started at about 1100 °C.

The main purpose of the present paper is study the efffect of alumina additions on the phase development, physical, and electrical properties of cordierite from rice husk silica. The structure was characterized by XRD and the microstructure was studied using SEM. Density, porosity, hardness and electrical resistivity were measured.

2. LITERATURE REVIEW

X-Ray Diffraction (XRD)

In order to identify the formed phases can be used XRD. The principle of this technique is to determine the interplanar spaces of every crystallographic phase. This can be possible using to the Bragg law:

$$n\lambda = 2\, d \sin\theta \qquad 1$$

where, n is the diffraction order, λ is the wavelength of the x-rays, d is the characteristic interplanar space between the crystal planes, and θ is the angle between the incident beam of x-rays and the normal to the reflecting plane. When the x-rays leave the crystal, the angle θ, it is possible to determine d, in a powder there is no order of the crystallographic planes, it means that it is possible to obtain a response of the most of the phases present (Ramachandra and Beaudoin, 2001). The obtained x-ray diffractogram are compared with the standard line pattens avalaible for various compounds in the Powder Diffraction File (PDF) database.

Density and Porosity

Density and porosity tests were performed to determine the quality of sample. The values of bulk density (B.D) and the apparent porosity (A.P) were determined in accordance with the Archimedes method (Australian Standard, 1989). The bulk density (D) and the apparent porosity (P%) were calculated using the following equations:

$$P(\%) = (W_s - W_d)/(W_s - W_{su}) \qquad 2$$

$$D = W_d/(W_d - W_{su}) \qquad 3$$

Where, W_d: weight of the dry sample after sintering (g), W_u: weight of the sample after immersing it in a distilled water and suspended in air through a balance (g), W_s : weight of the sample after immersing it in distilled water for 24 hrs (g).

Resistivity and Hardness

The conduction was ohmic in nature and the electrical conductivity was given by the equation (Pantea, *et.al*., 2001):

$$\sigma = L/R\, A \qquad 4$$

Where R is the resistance (Ω), A is the area of the sample (cm^2) and L is the sample thickness (cm).

Hardness may be defined as a material resistance to permanent identation. The depth of an identation in material created by a give force on a standarddized presser foot. The hardness can be obtained by a Vickers hardness tester. The hardness of the material is calculated from size of the impression produced under load by a piramid-shaped diamond indenter. The hardness of various samples was measured by using the formula:

$$Hv = 1.854\, (F/d)^2 \qquad 5$$

F is load (Kgf) and d is area of identation (mm^2).

3. EXPERIMENTAL METHOD

Raw husk used as a source of silica was from local rice milling industry in Lampung Province, Indonesia. Al_2O_3, MgO powders, KOH, HCl, and absolute alcohol (C_2H_5OH) were purchased from Merck (kGaA, Damstadt, Germany). Rice husk silica was obtained using alkali extraction method following the procedure reported in previous study (Sembiring, *et.al*., 2014). For extraction, 50 g dried and cleaned husk was mixed with 500 ml of 5% KOH solution in a beaker glass, folowed by boiling of the mixture for 30 minutes. The sol was acidified by dropwise addition of 5% HCl solution until conversion of the sol into gel was completed. The gel was oven dried at 110 ºC for eight hours and then ground into powder.

Preparation of cordierite was carried out by mixing raw materials with the composition of $MgO:Al_2O_3:SiO_2$ of 2:2:5 by mass, in accordance with the composition of cordierite as reported in previous studies (Simanjuntak, *et.al*., 2011). The raw materials were mixed with alcohol under magnetic stirring for 6 hours. After the completion of the mixing process, the mixture was filterred and the solid was oven dried at 110 ºC for eight hours to remove the adsorbed alcohol. The solid was ground into powder by mortar and sieved to obtain the powder with the size of 200 meshes.

Alumina was added to the cordierite powder in different proportions resulting in four batches as given in Table 1.

Table 1 Prepared cordierite-alumina ceramics batches

Batch Symbol	Alumina (%)	Cordierite (%)
C_0	0	100
C_{10}	10	90
C_{25}	25	75
C_{30}	30	70

The structure analysis was carried out using an automated Shimadzu XD-610 X-ray diffractometer at the National Agency for Nuclear Energy (BATAN), Serpong-Indonesia. Microstructural analysis was conducted with SEM Philips-XL, on polished and thermally etched samples. The examination of porosity and density was done according to Archimedes method (Australian Standard, 1989). A Zwick tester was used to measure the Vickers hardness, with three replicate measurements for each loading position.

4. RESULTS AND DISCUSSIONS

Fig. 1 displays the XRD pattern of the sample sintered at temperature of 1230 ºC and Fig. 2 (a-c) show the XRD patterns with different alumina content.

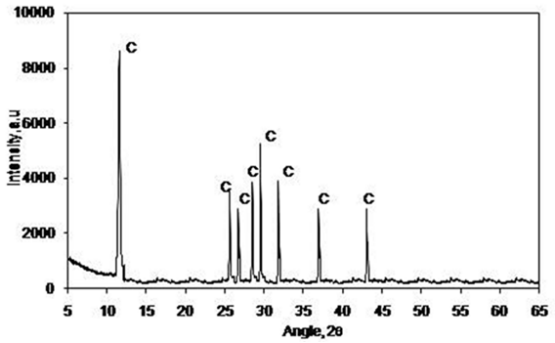

Fig. 1. The x-ray diffraction pattern of the sintered sample at temperature of 1230^{o}C, C= Cordierite.

The phases identified with the PDF diffraction lines using search-match method (Powder Diffraction File, 1997), clearly show the presence of alumina/Al_2O_3 (PDF-46-1212), α-cordierite/$Mg_2Al_4Si_5O_{18}$ (PDF-13-0294), spinel/$MgAl_2O_4$ (PDF-21-11520), cristobalite/SiO_2 (PDF-39-1425), and periclase/MgO (PDF-45-0946).

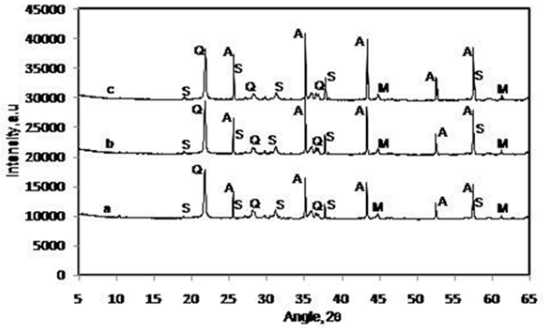

Fig. 2. The x-ray diffraction patterns of the sintered sample at temperature of 1230^{o}C with different alumina content (a) 10 %, (b) 25% and (c) 30 %, A= Alumina, S= Spinel, Q=Cristobalite, M= Periclase

As can be seen in the pattern in Fig. 1, only major cordierite phase was oberved. XRD analysis of the samples C_{10}, C_{25} and C_{30} (Fig. 2a-c) reveal the appearance of several phases of alumina, crystobalite, spinel and periclace. The peaks intensities of them increase with increasing alumina content.

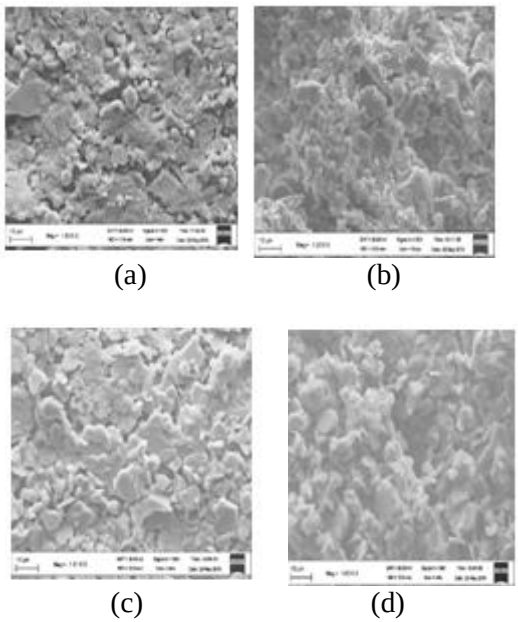

Fig. 3. The scanning electron microscopy (SEM) images of the samples with different alumina content (a) 0 %., (b) 10%., (c) 25 %., and (d) 30 %.

The morphology of the sintered samples was characterized using SEM. The images were shown in Fig. 3(a-d). SEM of sample C_0 (Fig. 3a) shows formation of cordierite as supported by XRD result in Fig 1. As revealed by the images in Figure 3a-c, the surface morphology of the samples is marked by different grain size and distribution. Adding 10 % alumina results the appearance of some grain boundaries with different size, which is obviously the clusters by large grains. The

large grains are most like alumina and crystobalite, while the middle and fine grains are spinel and periclase. Higher addition of alumina (25 and 30%) is most likely dominated by large grains composed of alumina and crystobalite clusters and covered some fine grains of spinel and periclace, which displays relatively very uniform surface with small grain sizes, and covered the entire surface. Increasing alumina content leads to suppres the grain growth of α-cordierite crystal indicated by XRD result (Figure 2a-c).

Fig. 4 shows the characteristics of density and porosity of the samples as a function of alumina content. The result reveals the density and porosity increased as alumina content increased.

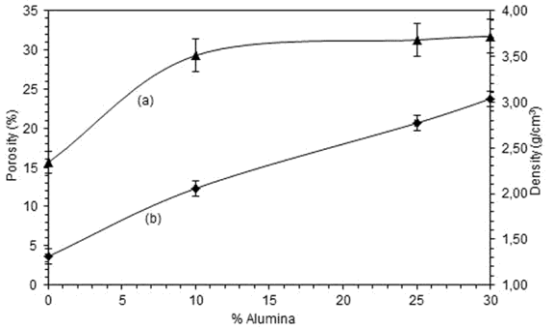

Fig. 4. Density (a) and Porosity (b) as a function of alumina content relative to cordierite

Fig. 5a-b shows the characteristics of hardness and electrical resistivity of the samples as a function of alumina content relative to cordierite. The result reveals the hardness increased with increasing the alumina content, while electrical resistivity the opposite is true.

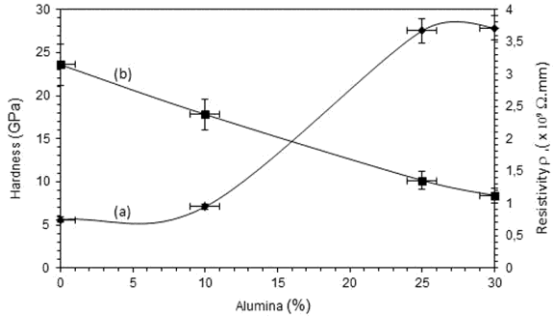

Fig. 5. Hardness (a) and resistivity (b) as a function of alumina content relative to cordierite

As shown in Fig. 5a, increased alumina content resulted in higher hardness, which is in agreement with the sample more compact and the decrease of the relative amount of cordierite (Fig. 2a-c). The electrical resistivity is decreased from alumina content of 0 to 30%. From practical point of view, this finding demonstrates that the electrical resistivity of samples be depended by phase composition, to adjust the electrical resistivity for specified application, such as insulator and conducting element.

5. CONCLUSIONS

The main results in this study are summarized as follows:

(i) Addition of alumina in the range from 10 to 30 % resulted several phases of alumina, crystobalite, spinel, periclase, and inhibited the cordierite growth.

(ii) The density, and hardness and were found to increase with increasing of alumina contain, as they are strongly influenced by microstructure of the material.

(iii) The electrical resistivity was observed to decrease with increasing of alumina contain, due to the influence of structure of the material.

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