UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF MULLITE-BASED CERAMICS FROM MALAYSIAN KAOLIN

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PREPARATION AND CHARACTERIZATION OF MULLITE-BASED CERAMICS FROM MALAYSIAN KAOLIN

By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Master of Science

PREPARATION AND CHARACTERIZATION OF MULLITE-BASED CERAMICS FROM MALAYSIAN KAOLIN

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April 2012

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Mullite ceramics are high performance ceramic due to its excellent high thermal shock resistance, chemical attack resistance, high hot strength and creep resistance properties. However, economical concerns in terms of cost and availability of mullite's raw materials have brought current efforts toward development of new inexpensive raw materials to synthesis mullite.

The first study investigates the effect of aluminum leaching during iron removal from kaolin to mullite. Heat-treated kaolin was obtained by heating natural kaolin at 400, 500, 600, 700, 800 and 900 °C. The heat-treated kaolin was then leached at 100 °C with 4 M, 3 M, 2 M, 1 M, 0.2 M solution of sulfuric acid and 0.2 M solution of oxalic acid. The dried samples were sintered to 1300 °C for 4

hour at a heating rate of 10 °C min^{-1}. X-ray diffractometry and differential thermal analysis were used to study the phase transformation of kaolin to mullite. It was found that 700 °C is the optimum preheat-treatment temperature to leach out iron and also aluminum for both types of the acids used. The majority of the 4 M sulfuric acid-treated kaolins formed the cristobalite phase when sintered. On the other hand, 1 M, 0.2 M sulfuric acid and 0.2 M oxalic acid leached heat-treated kaolin formed mullite and quartz phase after sintering.

Another study has been conducted to look into the possibility of using Malaysian kaolin and aluminum hydroxide to synthesize mullite. The treated Malaysian kaolin is mixed with aluminum hydroxide accordingly with the percentage of 10 %, 20 %, 30 %, 40 %, 50 %, 60 % and 80 % by weight. The study focuses on the effects of additional aluminum hydroxide on phase transformation of acid leached metakaolin clay. Finally, the percentage of mullite in the samples is compared with the percentage of aluminum hydroxide added. The results show that percentage of mullite in the treated kaolin can be increased by introducing additional of aluminum hydroxide. It was found that a correlation between percentage of aluminum hydroxide added and percentage of mullite formed can be established with a general equation. The study also reveals that the length of the acicular shape mullite crystals can be elongated from 2 up to 20 microns as the firing temperature increase from 1300 to 1600^{o}C.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah master sains

PENYEDIAAN DAN PENCIRIAN BAGI SERAMIK BERASASKAN MULLITE DARIPADA KAOLIN MALAYSIA

Oleh

CHOO THYE FOO

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Seramik mullite adalah seramik berprestasi tinggi disebabkan oleh sifatnya yang mempunyai rintangan kejutan terma yang tinggi, rintangan tindakbalas kimia, kekuatan pada suhu tinggi yang baik dan rintangan rayapan yang baik. Namun demikian, perhatian ekonomi dari segi kos dan ketersediaan bahan mentah untuk sintesis mullite, kini telah membawa usaha tertumpu kepada pembangunan bahan mentah baru yang lebih murah untuk sintesis mullite.

Kajian pertama mengkaji kesan pelarutlesapan aluminium semasa penyingkiran besi dari kaolin. Kaolin yang dirawat haba diperolehi dengan pemanasan kaolin semulajadi pada suhu 400, 500, 600, 700, 800 and 900 °C. Kaolin yang dirawat haba itu kemudian dilarutlesap pada suhu 100 °C dengan 4 M, 3 M, 2 M, 1 M, 0.2 M larutan asid sulfurik dan 0.2 M larutan asid oksalik. Sampel kering

tersebut kemudian dibakar pada 1300 °C selama 4 jam pada kadar pemanasan 10 °C min^{-1}. Teknik pembelauan sinar-X dan analisis terma telah digunakan untuk mengkaji pertukaran fasa kaolin kepada mullite. Kajian mendapati bahawa 700 °C merupakan suhu optimum rawatan haba bagi pelarutlesapan besi dan aluminium dengan penggunaan kedua-dua jenis asid. Majoriti kaolin yang dirawat dengan 4 M asid sulfurik membentuk fasa kristobalite selepas dibakar. Sebaliknya, kaolin yang dirawat dengan 1 M, 0.2 M asid sulfurik and 0.2 M asid oksalik membentuk fasa mullite dan kuartza selepas dibakar.

Satu lagi kajian telah dilakukan untuk melihat kemungkinan menggunakan kaolin Malaysia bersama aluminium hidroksida untuk menghasilkan mullite. Kaolin Malaysia yang telah dirawat dicampurkan dengan aluminium hidroksida mengikut peratusan keberatan 10 %, 20 %, 30 %, 40 %, 50 %, 60 % dan 80 %. Kajian tersebut mengkaji kesan penambahan aluminium hiroksida kepada pertukaran fasa bagi metakaolin yang telah dirawat oleh asid. Akhirnya, peratusan mullite pada sampel dibandingkan dengan peratusan aluminium hidroksida yang telah ditambahkan. Keputusan menunjukkan bahawa peratusan mullite di dalam kaolin yang dirawat boleh ditingkatkan dengan penambahan aluminium hidroksida. Kajian ini menemui bahawa satu korelasi antara peratusan aluminium hidroksida yang ditambahkan dengan peratusan mullite yang dihasilkan boleh dibentukkan dengan satu rumusan persamaan am. Kajian juga menunjuk bahawa kepanjangan hablur asikular mullite boleh dipanjangkan dari 2 ke 20 mikron apabila suhu pemanasan ditinggikan dari 1300 ke 1600°C.

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Without their support and contribution, this research project would not have been possible.

I certify that a Thesis Examination Committee has met on 10 April 2012 to conduct the final examination of Choo Thye Foo on his thesis entitled "Preparation and Characterisation of Mullite-based Ceramics from Malaysian Kaolin" in accordance with the Universities and University colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Degree of Master of Science.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

CHOO THYE FOO

Date: 10 April 2012

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LIST OF ABBREVIATION

%	Percentage
°C	Degree Celsius
Al_2O_3	Alumina
$Al_2Si_2O_5(OH)_4$	Kaolinite
cm	Centimetre
Fe_2O_3	Iron Oxide
g	gram
H_2O	Water
I_{hkl}	Bragg intensity
K_2O	Potash
mm	Millimetre
mol	Mole
M	Molar
MPa	Mega Pascal
Na_2O	Sodium oxide
rpm	Revolutions per minute
SiO_2	Silica
TiO_2	Titanium Dioxide
Wt%	Weight Percent

CHAPTER 1

INTRODUCTION

1.1 Introduction

Mullite is the mineralogical name given to the only chemically stable intermediate phase in the silica SiO_2 – alumina Al_2O_3 system, (Schneider and Komarneni, 2005). Mullite is commonly denoted as $3Al_2O_3 \cdot 2SiO_2$ (i.e. 60 mol% Al_2O_3). However it is actually a solid solution with the equilibrium composition limits of 60-63 mol% Al_2O_3 below 1600 ^oC (Aramaki and Roy 1962). Mullite is widely studied because it exhibits some properties such as thermal shock resistance, chemical attack resistance, creep resistance and high hot strength properties. Some papers concerning the used of aluminum-silicate minerals to produce mullite have been published. For example, mullite prepared from fly ash coated with aluminum hydroxide (Dong et al., 2008), mullite prepared from a mixture of natural bauxite and industrial waste fly ash (Dong et al., 2008), mullite prepared from clays and clay-based vitreous ceramic (Lee et al., 2008), mullite prepared from slate sludge and aluminum-containing residues (Oliveira et al., 2008).

Although mullite can be synthesized through different starting materials such as the materials mentioned above, its preparation from clay remains the most economical way. Kaolin the most common clay used to produce mullite (Lee and Iqbal, 2008), is a soft, white plastic clay consisting mainly of mineral kaolinite, a hydrated aluminum silicate $Al_2Si_2O_5(OH)_4$. However, kaolin clay contains large amount of SiO_2, mainly in the form of quartz crystals and amorphous silica. When kaolin clay undergoes sintering, some of these SiO_2 will be used for mullite formation and the remaining will be converted to cristobalite. Generally, percentage of mullite can be increased by introducing additional aluminum source into kaolin clay before mullitization phase transformation; this aluminum source will combine with the remaining free SiO_2 to form additional mullite. Some research has been done to increase the percentage of mullite, for example, mullite prepared from kaolin clay (Viswabaskaran et al., 2003) and mullite prepared by the reaction sintering of kaolinite and alumina. (Chen et al., 2000).

In nature, kaolin contains impurities, mainly iron, that may alter the properties and hence the performance of the products derived from it. These impurities have to be removed prior to the use of the material. The most common and effective leaching method is by the reaction of mineral acids, but this may further increase SiO_2 percentage in the kaolin, which renders it more difficult to fully convert to mullite.

The present study is to explore the sulfuric acid H_2SO_4 leached metakaolin clay combined with aluminum hydroxide $Al(OH)_3$ to synthesize mullite. There is no study on using H_2SO_4 leached metakaolin as SiO_2 source. H_2SO_4 leaching on metakaolin serves two purposes: first, it is to have the iron impurities remove; and second, it is desirable to obtain a high surface area metakaolin that favor Al atomic diffusion in mullite synthesis. $Al(OH)_3$ is used to react with H_2SO_4 leached metakaolin clay to synthesize mullite instead of pure alumina, this is because $Al(OH)_3$ has low hardness which can lower the possibility of introducing impurities during milling. Apart from that, mullite yield has not been studied in all the details in previous studies, for this reason this study will established a correlation between percent of $Al(OH)_3$ added and percent of mullite formed.

1.2 Objective of Study

This study is conducted to accomplish some predefined objectives. These objectives are:

I. To study the optimum condition of H_2SO_4 leaching process for metakaolin clay and the effects of H_2SO_4 leaching on aluminum removal and consequent phase transformation of sintered product.

II. To increase the percentage of mullite by introducing additional aluminum hydroxide and establish correlation between percent of aluminum hydroxide added and percent of mullite formed.

1.3 Scope of Study

This study focuses on preparation of low iron mullite-based ceramics from Malaysian kaolin. The Malaysian kaolin contains iron impurities that require leaching process to remove them. The Malaysian kaolin needs to be heat transformed to metakaolin first to ease the leaching process. With regard to this matter, the optimum condition for leaching process is studied. For the first objective, six samples of Malaysian kaolin that were subjected to heat treatment at 400°C, 500°C, 600°C, 700°C, 800°C and 900°C for 4 hours, are leached with 4M, 3M, 2M, 1M, 0.2M H_2SO_4, and 0.2M oxalic acid at 100°C for 4 hours respectively. Chemical analysis tests and crystalline phase identification are conducted on the samples to study the effects of leaching on iron, aluminum removal and consequent phase transformation of the sintered product.

For the second objective, 3M and 2M H_2SO_4 leached kaolin that were dry-ground together with 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60wt% and 80 wt% of aluminum hydroxide using planetary ball-mill are fired at 1300^{o}C and 1600^{o}C for 4 hours. The scanning electron microscope SEM analysis was used to study the surface morphologies of the sample with various percentage of aluminum hydroxide. The profound effect of sintering temperature on mullite's crystal size was also studied. Crystalline phase composition analysis using Rietveld analysis is conducted on the samples to establish correlation between percent of aluminum hydroxide added and percent of mullite formed.

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