



UNIVERSITI PUTRA MALAYSIA

***MODIFIED CENOSPHERES AS NON-SACRIFICIAL PORE-FORMING
AGENT FOR DEVELOPMENT OF POROUS MULLITE CERAMICS
ENTIRELY FROM INDUSTRIAL WASTES***

CHOO THYE FOO

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By

CHOO THYE FOO

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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Doctor of Philosophy**

August 2021

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

MODIFIED CENOSPHERES AS NON-SACRIFICIAL PORE-FORMING AGENT FOR DEVELOPMENT OF POROUS MULLITE CERAMICS ENTIRELY FROM INDUSTRIAL WASTES

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CHOO THYE FOO

August 2021

**Chairman : Associate Professor Mohamad Amran bin Mohd Salleh, PhD
Institute : Advanced Technology**

Mullite is a widely used ceramic because it exhibits some advantageous properties such as thermal shock resistance, chemical resistance, creep resistance, high hot strength and low coefficient of thermal expansion. Driven by the need for low-cost and environmentally friendly alternatives, extensive research on the utilization of low-cost materials to produce mullite ceramics is crucial. In this study, mullite ceramics were produced entirely from aluminum dross (AD) and coal fly ash (CFA) industrial wastes. Both wastes were mixed together in different weight ratio, subsequently compacted and sintered. The effects of the sintering temperature, acid leaching and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio on the chemical, physical, thermal expansion properties of the samples were characterized in detail. The results showed that appropriate mixing ratio and acid leaching had positive effects on the mineralogy, crystallinity, and macromorphology of sintered samples. At sintering temperature of 1500 °C, high mullite content ceramics with good crystallinity were produced. The resultant ceramics exhibited excellent thermal expansion properties with coefficient of thermal expansion (CTE) values ranging from 4.0 to 5.9 $\times 10^{-6}$ °C⁻¹. Modified cenospheres were used as non-sacrificial pore-forming agent to produce porous mullite ceramics. The results showed that addition of modified cenospheres leads to the increment of both total porosity and closed porosity, with the reduction of open porosity. Addition of 40 wt% of modified cenospheres to the mullite precursor, the resultant porous mullite ceramic has a total porosity of 50.2%, thermal conductivity of 1.28 Wm⁻¹K⁻¹, linear shrinkage of 4%, and biaxial flexural strength of 45.9 MPa. The mullite precursor was also used to produce high-temperature porous mullite washcoat. Results showed that the precursor transformed to a hierarchical porous microstructure assembled by large interlocked acicular mullite crystals. The specific surface area of the washcoat was 4.85 m²g⁻¹, which comparable to the other high-temperature washcoats.

This study offers the potential of using these industrial wastes as a sustainable alternative raw material in the development of mullite ceramics.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**CENOSPHERES TERUBAHSUAI SEBAGAI AGEN PEMBENTUKAN LIANG
TANPA LESAP UNTUK PEMBANGUNAN SERAMIK MULIT BERLIANG
DARIPADA SISA-SISA INDUSTRI SEPENUHNYA**

Oleh

CHOO THYE FOO

Ogos 2021

Pengerusi : Profesor Madya Mohamad Amran bin Mohd Salleh, PhD
Institut : Teknologi Maju

Mulit adalah seramik yang digunakan secara meluas kerana ia mempunyai ciri-ciri kelebihan seperti ketahanan kejutan terma, ketahanan kimia, ketahanan rayapan, kekuatan panas yang tinggi dan pekali pengembangan haba yang rendah. Didorong oleh permintaan bahan alternatif yang murah dan mesra alam, penyelidikan yang mendalam mengenai penggunaan bahan kos rendah untuk penghasilan mulit adalah sangat penting. Dalam kajian ini, Seramik mulit dihasilkan sepenuhnya daripada sisa-sisa industri seperti serdak aluminium dan abu terbang arang batu. Kedua-dua sisa ini dicampurkan dengan nisbah keberatan yang berbeza, kemudian dipadat dan disinter. Kesan-kesan suhu sinter, rawatan asid dan nisbah $\text{Al}_2\text{O}_3/\text{SiO}_2$ terhadap sifat kimia, fizikal, dan pengembangan haba sampel dikaji dengan terperinci. Hasil kajian menunjukkan bahawa nisbah campuran yang sesuai dan rawatan asid memberi kesan positif terhadap mineralogi, kehabluran, dan makromorfologi sampel yang disinter. Pada suhu sinter $1500\text{ }^\circ\text{C}$, seramik ber Kandungan mulit yang tinggi dengan tahap kehabluran yang baik telah dihasilkan. Seramik tersebut mempamerkan sifat pengembangan haba yang sangat baik dengan nilai pekali pengembangan haba dari 4.0 hingga $5.9 \times 10^{-6}\text{ }^\circ\text{C}^{-1}$. Cenospheres terubahsuai telah digunakan sebagai agen pembentukan liang tanpa lesap untuk menghasilkan seramik mulit berliang. Hasil kajian menunjukkan bahawa penambahan cenospheres terubahsuai meningkatkan jumlah liang dan liang tertutup, di samping itu mengurangkan liang terbuka. Penambahan 40 wt% cenospheres terubahsuai menghasilkan seramik mulit berliang yang mempunyai jumlah liang sebanyak 50.2%, kekonduksian haba sebanyak $1.28\text{ Wm}^{-1}\text{K}^{-1}$, pengecutan linear sebanyak 4%, dan kekuatan lenturan biaksial sebanyak 45.9 MPa. Prekursor mulit juga telah digunakan untuk menghasilkan pembawa mangkin mulit berliang suhu-tinggi. Hasil kajian menunjukkan bahawa prekursor bertukar kepada satu mikrostruktur berliang hierarki yang dibentuk oleh kristal mulit asikular besar yang berpautan. Keluasan permukaan spesifik pembawa

mangkin multilayer adalah $4.85 \text{ m}^2\text{g}^{-1}$, dimana setanding dengan pembawa mangkin suhu tinggi yang lain. Kajian ini menawarkan potensi menggunakan sisa-sisa industri ini sebagai bahan mentah alternatif yang mampan dalam penghasilan seramik multilayer.



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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mohamad Amran bin Mohd Salleh, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Khamirul Amin bin Matori, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Suraya binti Abdul Rashid, PhD

Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Kok Kuan Ying, PhD

Research officer
Malaysian Nuclear Agency
Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Signature: _____
Name of Chairman
of Supervisory
Committee: Associate Professor
Dr. Mohamad Amran bin Mohd Salleh

Signature: _____
Name of Member
of Supervisory
Committee: Associate Professor
Dr. Khamirul bin Amin Matori

Signature: _____
Name of Member
of Supervisory
Committee: Professor
Dr. Suraya binti Abdul Rashid

Signature: _____
Name of Member
of Supervisory
Committee: Dr. Kok Kuan Ying

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LIST OF ABBREVIATIONS

EDXRF	Energy dispersive X-ray fluorescence
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscope
EDS	Energy dispersive spectroscopy
CTE	Coefficient of thermal expansion
TG-DSC	thermogravimetry and differential scanning calorimetry analysis
BET	Brunauer-Emmer-Teller
BJH	Barrett-Joyner-Halenda
rpm	Revolutions per minute
MPa	Mega Pascal
CFA	Coal fly ash
AD	Aluminum dross
MP	Mullite precursor
P/P_0	Relative pressure
ICDD	International Centre for Diffraction Data
d50	average particle size
IUPAC	International Union of Pure and Applied Chemistry

CHAPTER 1

INTRODUCTION

1.1 Brief introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the chemically stable intermediate phase in the silica – alumina system. It is a widely used ceramic because it exhibits some advantageous properties such as thermal shock resistance, chemical attack resistance, creep resistance, high hot strength and low coefficient of thermal expansion. Driven by the need for low-cost and environmentally friendly alternatives, many research efforts have used a variety of industrial wastes as starting materials to produce mullite ceramics.

One of the industrial wastes being used as starting materials to produce mullite ceramics is coal fly ash (CFA). Most of the past efforts on CFA utilization in mullite production have been focused on the preparation of mullite ceramic and its composites with addition of other aluminum sources such as alumina, aluminum hydroxide, aluminum sulfate and bauxite. This is because the SiO_2 content in CFA is often excessive for the amount required for the preparation of mullite. Furthermore, excessive SiO_2 associated with impurities can lead to a sample deformation or meltdown in high-temperature sintering. Generally, percentage of mullite in CFA can be increased by introducing additional aluminum source before mullitization phase transformation takes place; this aluminum source will then combine with the remaining free SiO_2 in CFA to form additional mullite. Although all these processes from the previous studies are feasible, they utilized CFA as an alternative silica source, but the aluminum source they utilized is not a waste, which defeats the purpose of using industrial waste in the first place. Aluminum Dross (AD) is a waste product, which produced from secondary aluminum refining. This waste product has high content of Al_2O_3 . This makes AD a good candidate waste material to mix with CFA to produce mullite.

Past and current development of porous mullite have been focused on producing mullite ceramics with high permeability, in other words, the majority of the pores are technically open, functioning as small channels. The open pores and pore channels formation are related to pyrolysis; burnout; sublimation of sacrificial pore-forming agent and binder. Generally, close pores are difficult to form and control using these methods. A so-called non-sacrificial pore-forming agent is different from the traditional sacrificial pore-forming agent. This type of pore-forming agent is based on its ability to increase the porosity of the matrix by its internal hollow volumes, and with little or no disintegration in the process. Therefore, non-sacrificial pore-forming agent is more suitable to produce porous mullite ceramic with majority closed pores. Coal fly ash cenospheres are

aluminosilicate hollow spheres with high silica and alumina content. Cenospheres have been utilized as non-sacrificial pore-forming agent in some low-temperature applications. However, it has not yet been successfully proven to be used in high-temperature applications. Therefore, it is crucial to understand the thermal behaviors of the cenospheres at high temperatures, so that it can be used as a non-sacrificial pore-forming agent for the porous mullite ceramics fabrication.

Monolith washcoat is the crucial component of a catalyst support. It is where the catalytic reactions take place, as the main function of the washcoat is to provide high contact surface area between the catalyst and reacting gases for high reaction rates. Additionally, the washcoat has to be thermally stable at working temperatures. Mullite appears to be promising candidate for this high-temperature (>1000 °C) washcoat application. Therefore, it is also important to investigate the feasibility of using aluminum dross and coal fly ash derived mullite precursor in the production of mullite washcoat.

1.2 Problem statements

Mullite is a promising advanced ceramic material. It can be produced from a variety of raw materials, namely chemicals, natural minerals, industrial wastes, or a combination of them. Over the years, manufacturing cost reduction efforts have gained much attention. The utilization of low-cost raw materials for ceramics production has become more desirable. Although some studies concerning about the use of low-cost materials to produce mullite ceramic had been published. But the utilization of 100% wastes to produce high-content mullite ceramic is still unachievable.

Coal fly ash (CFA) is a by-product in coal-fired powerplant. CFA is utilized in industry as a substitute for fine aggregates in cement and concrete, in bricks and ceramic tiles, as filler in plastics and paints. But the utilization rate of the fly ash is rather low. In general, CFA has pozzolanic properties and its major mineral phases are silica and alumina in the form of quartz and mullite. Aluminum Dross (AD) is also a waste product, it produced from secondary aluminum refining. Currently, AD is processed in rotary kilns to recover the Al, and the resultant salt cake is sent to landfills. Although it is sealed to prevent from leaching, the potential for leaching still exists. Illegal dumping of this toxic waste can lead to serious environmental problem which could harm human health and the environment due to the fluorides and other salts contents in the salt cake. Owing to the high content of useful minerals in CFA and AD, it is economically viable to recover these minerals for useful industrial applications. Furthermore, energy consumed in the waste treatment can be saved if the wastes could be developed as a new material.

Most of the porous mullite ceramics have high permeability, in other words, the majority of the pores are technically open, functioning as small channels. This type of porous ceramics is not suitable for refractory. The penetration of hot flowing gases and liquid melt in the pores may cause refractory failure, and toxic gas at high pressure that leak through the pores may cause safety hazard. Therefore, the development of porous mullite ceramics with less open pores is crucial for refractory.

1.3 Scope of study

In first part of this study, coal fly ash (CFA) and aluminum dross (AD) were investigated as the sole raw materials in the production of mullite-based ceramics. Both of the industrial wastes were mixed together in different weight ratio, subsequently compacted and sintered. The effects of the sintering temperature, acid leaching and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio on the chemical, physical, thermal expansion properties of the samples were characterized in detail. The chemical composition was determined by energy dispersive X-ray fluorescence (EDXRF) using a Shimadzu EDX-7000. X-ray diffraction (XRD) pattern at room temperature for the sample was recorded by using PANalytical X'Pert PRO using monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) and phase composition was analyzed by Rietveld refinement method. The evaluation of relative degree of crystallinity of the samples was estimated from the measured X-ray intensity. The microstructure was characterized using a GeminiSEM 500 FESEM (Zeiss, Germany) equipped with an X-Max EDS detector (Oxford Instruments, UK). A Netzsch DIL 402C Dilatometer was used to measure linear thermal expansion of the sintered samples from room temperature to $1000 \text{ }^\circ\text{C}$.

In second part of the study, the influence of temperature on morphology, phase transformations and thermal expansions of coal fly ash cenospheres was investigated. The cenospheres were extracted from coal fly ash and heat-treated at 800 , 1000 , 1200 and $1400 \text{ }^\circ\text{C}$ for 2 hours. The cenospheres and heat-treated cenospheres (1000 , 1200 and $1400 \text{ }^\circ\text{C}$) were characterized by X-ray diffraction using PANalytical X'Pert PRO. The cenospheres were also characterized by a STA-449-F3 Jupiter simultaneous thermal analyzer (Netzsch, Germany) for their temperature-dependent phase transitions. The cenospheres and heat-treated cenospheres (1000 , 1200 and $1400 \text{ }^\circ\text{C}$) were characterized using a GeminiSEM 500 FESEM (Zeiss, Germany) equipped with an X-Max EDS detector (Oxford Instruments, UK). The differences between particle morphology, shape and size were analyzed. The $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of mullite crystallites was computed based on the EDS results. A Netzsch DIL 402C Dilatometer was used to measure the linear thermal expansion of the powder samples in an alumina sample container from 100 to $1000 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$. The length change was recorded with a dense α -alumina as reference sample.

In third part of the study, porous mullite ceramics were synthesized using the mullite precursor produced from the first part of the study together with modified cenospheres as a non-sacrificial pore-forming agent. In this part of the study, the effects of surface modification on cenospheres and the performance of the resultant porous mullite ceramics will be investigated. The microstructures of the samples were characterized using a Zeiss GeminiSEM 500 field emission scanning electron microscope (FESEM). Chemical composition was determined by energy dispersive X-ray fluorescence (EDXRF) using a Shimadzu EDX-7000. X-ray diffraction (XRD) patterns were recorded by using PANalytical X'Pert PRO using monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) and phase composition were analyzed by Rietveld refinement method. The degree of crystallinity was estimated from the measured X-ray intensity. Thermal conductivity was measured at room temperature using Hot Disk TPS 2500S thermal conductivity analyzer via transient plane source method.

In fourth and last part of the study, the feasibility of the aluminum dross and coal fly ash derived mullite precursor in the production of mullite washcoat was investigated. The precursor was made into slurry using deionized water and dip coated on flat alumina substrates and fired at $1200 \text{ }^\circ\text{C}$ and $1500 \text{ }^\circ\text{C}$ for 4 hours. The chemical composition of the starting materials was determined by energy dispersive X-ray fluorescence (EDXRF) using a Shimadzu EDX-7000. Particle size distributions of the powders were measured with the aid of a laser particle size analyzer (Microtrac X100). Zeiss GeminiSEM 500 FESEM was used for the study of the morphology of the starting mullite precursor and the sintered mullite washcoat on alumina substrates. The X-ray diffraction (XRD) pattern at room temperature for the samples were recorded by using PANalytical X'Pert PRO using monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$), and the phase composition was analyzed by Rietveld refinement method. N_2 physical adsorption-desorption isotherm of the washcoat was obtained with a surface area analyzer (Quantachrome Autosorb-1-C) at 77 K .

1.4 Objectives of Study

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

- I. To synthesize and characterize mullite ceramics developed from coal fly ash (CFA) and aluminum dross (AD), and investigate the effects of the sintering temperature, acid leaching and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio on the chemical, physical, thermal expansion properties of the samples.
- II. To investigate the morphology, phase transformations and thermal expansions of the cenospheres at high temperatures, and assess the potential of cenospheres as a non-sacrificial pore-forming agent for porous ceramic fabrication.

- III. To synthesize and characterize porous mullite ceramics using the waste derived mullite precursor and modified cenospheres as a non-sacrificial pore-forming agent, and investigate the effects of cenospheres surface modification on the pore characteristic and thermal conductivity of the resultant porous mullite ceramics.
- IV. To synthesize mullite washcoat using the waste derived mullite precursor, and characterize the surface properties and pore size distribution of the mullite washcoat.



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