Study on Kaolin Geopolymer Ceramic using Powder Metallurgy Method

by

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A thesis submitted in partial fulfilment of the requirements for the degree of Master of Science in Materials Engineering

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2016

ACKNOWLEDGEMENT

I take this opportunity to express my deepest gratitude to the people who have been involved in successful completion of this thesis. I owe sincere and earnest thankful to my dear project supervisors, Assoc. Prof. Dr. Mohd Mustafa Al Bakri Abdullah and Assoc. Prof. Dr. Che Mohd Ruzaidi Ghazali for their tremendous help, critics, support and encouragement. Without his guidance, this project would not be materialized.

I would like to thank all of the laboratory technicians at UniMAP for their assistance throughout the experiment. Their opinion towards the better solution for certain problem was much appreciated.

On top of that, I felt highly indebted to my parents, Mr. Jaya Yaacob and Mrs. Che Karimah Mat for their continuous support and keeping me harmonious upon the completion of this project.

Last but not least, I am obliged to many of my colleagues and everyone who supported me when I am not in my best condition. I am grateful for their constant support and help.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
KGC	Kaolin geopolymer ceramic
BET	Branauer-Emmet-Teller
MPa	Mega Pascals
ICSD	Inorganic Crystal Structure Database
PS	Polysialate
PSA	Particle Size Analyzer
PSS	Polysialate-siloxo
PSDS	Polysialate-disoloxo
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectroscopy
LOI	Loss on Ignition
Wt.%	Weight per cent
X_{50}	Mean particle size

Kajian Seramik Geopolimer Kaolin menggunakan Kaedah Metalurgi Serbuk

ABSTRAK

Geopolimer adalah bahan polimer organik disintesis daripada pembubaran dan polikondensasi aluminosilikit dalam larutan alkali pada suhu ambien dan menghasilkan satu polimer amorfus dan berangka tiga dimensi. Geopolimer menjadi perhatian kerana mesra alam sekitar, kos yang rendah, kekuatan awal yang tinggi, ketahanan dan rintangan kimia yang tinggi. Kaolin digunakan sebagai sumber aluminosilikat di dalam kajian ini. Pemilihan kaolin menawarkan beberapa kelebihan ke arah bahan-bahan sumber biasa digunakan dalam geopolimer seperti metakaolin. Proses kehilangan air menyebabkan penguraian kristal kaolinit kepada struktur separa tersusun untuk menghasilkan metakaolin. Tindak balas ini memerlukan pengkalsinan kaolin pada suhu antara 500 °C - 900 °C. Pengkalsinan kaolin menghadkan aplikasi komersil metakaolin kerana pertambahan kos dan penggunaan tenaga yang banyak. Teknologi terbaru telah memberi tumpuan kepada memperluaskan penggunaan geopolimer dengan penukaran kepada seramik apabila dipanaskan pada suhu tinggi. Dalam usaha untuk mengatasi masalah yang timbul, kaedah yang berkesan adalah untuk menggunakan kaedah metalurgi serbuk dimana serbuk geopolimer dimampatkan dan disinter. Terdapat tiga parameter yang terlibat untuk menghasilkan seramik kaolin geopolimer dengan sifat-sifat yang optimum iaitu kepekatan NaOH, nisbah Na_2SiO_3 / NaOH dan suhu pensinteran. Sifat dan ciri-ciri seramik kaolin dan seramik geopolimer kaolin telah dijalankan menggunakan kekuatan lenturan, ketumpatan, ujian penyerapan air, analisis fasa dan analisis morfologi. Hasil kajian menunjukkan bahawa NaOH kemolaran daripada 12 M, nisbah Na_2SiO_3/NaOH 0.24:1 dan suhu pensinteran 1200 °C memberi kekuatan lenturan tertinggi 88.47 MPa, ketumpatan 2.13 g/cm^3 dan ujian penyerapan air sebanyak 1.2 %. Analisis fasa menunjukkan bahawa fasa nepheline yang tertinggi menyumbang kepada kekuatan yang tinggi terhadap seramik geopolimer kaolin. Analisis mikrostruktur menunjukkan bahawa pensinteran geopolimer pada 1200 °C menyebabkan pembentukan liang disebabkan oleh penguraian bahan ketika melalui proses sinter. Sebagai kesimpulan, kajian ini telah memberi pemahaman tentang bagaimana kepekatan NaOH, nisbah Na_2SiO_3/NaOH dan suhu pensinteran mempengaruhi sifat (kekuatan lenturan, ketumpatan, pengecutan volumetrik dan ujian penyerapan air) dan ciri-ciri (mikrostrukstur dan fasa) seramik kaolin geopolimer. Untuk cadangan kajian pada masa hadapan, sumber aluminosilikat yang lain boleh dicadangkan untuk dijadikan sebagai seramik geopolimer.

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ABSTRACT

Geopolymer is an inorganic polymeric material synthesized from the dissolution and polycondensation of aluminosilicates in alkaline solutions at ambient temperature yielding an amorphous, three-dimensional polymeric framework. Geopolymers become an interest due to environmental friendly, low cost production, high early strength, durability and high chemical resistance. Kaolin is used as the aluminosilicate source in this study. The selection of kaolin offers a few advantages towards the common source materials used in geopolymer such as metakaolin. Dehydroxylation cause the decomposition of kaolinite crystals to a partially disordered structure to produce metakaolin. This reaction requires calcining of kaolin at temperatures between 500 °C - 900 °C. Calcining kaolin limits the commercial application of metakaolin due to the added cost and consume much energy. Recent technology has been focusing on widening the application of geopolymer by conversion to ceramics upon heating to higher temperature. In order to overcome problem arise, the effective method was to use powder metallurgy method whereby to sinter ground and compressed geopolymer powder. There are three parameters that involved to produce kaolin geopolymer ceramics with optimum properties which are NaOH concentration, Na_2SiO_3/NaOH ratios and sintering temperatures. The properties and characterization of kaolin ceramic and kaolin geopolymer ceramic has been done using a flexural strength, density measurement, water absorption measurement, phase analysis and microstructural analysis. Results showed that NaOH molarity of 12 M, Na_2SiO_3/NaOH ratio of 0.24:1 and sintering temperature of 1200 °C gives the highest flexural strength of 88.47 MPa, a density of 2.13 g/cm^3 and water absorption of 1.2 %. Phase analysis show that the highest peak intensity of nepheline contributed to this high strength of kaolin geopolymer ceramic. Microstructural analysis show that sintering the geopolymer to 1200 °C resulted in the formation of pores possibly due to the decomposition of the material on sintering. As a conclusion, this study provides a better understanding on how NaOH concentration, Na_2SiO_3/NaOH ratios and sintering temperature influence the properties (flexural strength, density measurement, volumetric shrinkage measurement and water absorption measurement) and characteristics (microstructure and phase) of kaolin geopolymer ceramic. For future research, another aluminosilicate materials can be proposed for geopolymer ceramic.

CHAPTER 1

INTRODUCTION

1.1 Background

Inorganic polymers, commonly referred as geopolymers are a new class of materials and first developed by Professor Joseph Davidovits in 1978 Davidovits (1991). Recently discovered geopolymers are ceramic-like materials produced by geopolymerization reaction that use aluminosilicate materials such as kaolin and an alkaline activating solution such as sodium hydroxide as the primary raw materials (Bakharev, 2006). Geopolymerization reaction involves the dissolution and condensation process that occurs at room temperature. However, geopolymers can be converted to ceramic through sintering to high temperatures up to 1400 °C. Crystalline phases are formed at high temperatures and sintering result in the formation of ceramic products (Kuenzel et al., 2013). Therefore, geopolymer technology provides a new route to fabricate advanced ceramics (He et al., 2013). Geopolymer paste can be cast into designated shape and allowed to cure prior to sintering, with the formation of crystalline phases and improved properties.

Various aluminosilicate source materials have been utilized in the manufacturing of geopolymers. Fly ash is one of the example that have been used as aluminosilicate source due to its nature of high reactivity and able to produce high strength product (Görhan &

Kürklü, 2014). Ryu et al. (2013) has developed cementless geopolymer concrete using fly ash activated with sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3).

The geopolymers produced with the higher molarity of NaOH as an alkali activator appeared to provide higher compressive strength. Jaarsveld et al. (2002) stated that curing temperature greatly affects the final compressive strength and curing at higher temperature for more than a couple of hours positively affect the development of compressive strength. Metakaolin is produced from the heat treatment of kaolinite clay through calcination. When kaolinite is heated in the temperature range of 550 °C - 900 °C, H^+ ions are removed to form metakaolin (Chandrasekhar, 1996). Silva et al. (2007) prepared geopolymer using metakaolin with NaOH and Na_2SiO_3. Increasing of silicon oxide/aluminium oxide (SiO_2/Al_2O_3) molar ratios up to 3.4 - 3.8 leads to an increase in mechanical strength. Rovnanik (2010) has stated that curing temperature has an essential effect on the setting and heat setting of geopolymers by utilized metakaolin.

Depending on the raw materials selection and processing conditions, geopolymers can exhibit excellent compressive strength (Hardjito & Rangan, 2005), fire resistance (Duxson et al., 2007b; Kovalchuk & Krivenko, 2009) and toxic waste immobilization (Aly et al., 2008; Jaarsveld & Deventer, 1996). The strength of geopolymers depends on the nature of source materials. Calcined source materials for example metakaolin yield higher compressive strength compared to uncalcined materials such as kaolin. Rahier et al. (1996) has achieved high compressive strength of more than 60 MPa in his research. Barbosa and Mackenzie (2003a) studied the high temperature ability of geopolymer materials and found that geopolymers with high aluminium/silica (Al/Si) ratio have high thermal stability with melting points in the range of 1400 °C. The K-PS geopolymer retained their dimensional integrity and showed no sign of melting after heating at 1400 °C. Kong et al. (2007) compared the performance between fly ash and metakaolin geopolymers at elevated temperatures up to 800 °C and found that fly ash geopolymers has increased strength while metakaolin decreased in strength.

Geopolymers are already being applied in many fields such as geopolymer cement and concrete. Davidovits (1994) has recorded 28 days compressive strength of 70 MPa - 100 MPa using geopolymer concrete. Geopolymer has made its way in high temperature and fireproof application. Davidovits (1991) described geopolymer resins to have very low viscocity, geopolymers could harden like thermosetting organic resins and can be used to temperature up to 1000 °C.

1.2 Problem Statement

Over the years, kaolin has been a very important ingredient in ceramics industry. However, the use of kaolin in producing ceramics through the conventional method requires high temperature (up to 1400 °C) processing to obtain high performance. In order to overcome this problem, geopolymer technology can be used to produce high performance ceramics at a slightly lower temperature.

A previous study has been utilized metakaolin as the aluminosilicate source (Xie et al., 2010). However, the use of kaolin in geopolymer ceramics has not been studied. Kaolin has been chosen as the aluminosilicate source for the geopolymer synthesis in this study because it is readily available starting materials. Besides, raw kaolin was considered for the synthesis of geopolymers without a preliminary thermal activation, in order to limit the overall energy demand for calcination in the way of sustainable development (Heah et al., 2011; Heah et al., 2012b).

1.3 Objectives

This thesis documents the work undertaken to fabricate geopolymer ceramic by exposing the geopolymer to elevated temperatures. The highlight of this research work is to use the powder metallurgy method in producing high strength geopolymer ceramics. The use of kaolin as an aluminosilicate source material for the synthesis of geopolymers also will be investigated. The specific objectives of the research are:

1. To determine the optimum sodium hydroxide concentration based on flexural strength in producing kaolin geopolymer ceramic.
2. To identify the optimum alkaline activator ratios based on flexural strength in fabricating the kaolin geopolymer ceramic.
3. To obtain the suitable sintering temperature based on flexural strength for kaolin geopolymer ceramic.

1.4 Scope of Research

The experimental work will begin with the characterization of the aluminosilicate source used which is kaolin. The characterization includes the use of X-ray Fluorescence (XRF) to assess the chemical composition, X-ray Diffraction (XRD) to identify the present phase, particle size analysis (PSA) to obtain the size of kaolin particles used and Scanning Electron Microscope (SEM) to study the morphology of the microstructure of kaolin. The geopolymers will be synthesized based on three important parameters which are sodium hydroxide concentration, sodium silicate to sodium hydroxide ratio and sintering temperatures to acquire the optimum mechanical properties.

The geopolymers that will be exposed to elevated temperatures will be characterized by a wide range of testing techniques. Shrinkage behaviour was measured before and after sintering. Flexural strength will be carried out as the main testing in order to evaluate the optimum key parameters for the fabrication of geopolymer ceramics. Phase analysis is used to determine the crystalline phase of the samples as well as recognition of amorphous materials in geopolymers. Microstructural analysis will be conducted to monitor the microstructural development of the geopolymer such as cracks, sample morphology, porosity and to identify reacted/unreacted regions. The details of the work flow for this research is shown in Figure 1.1.

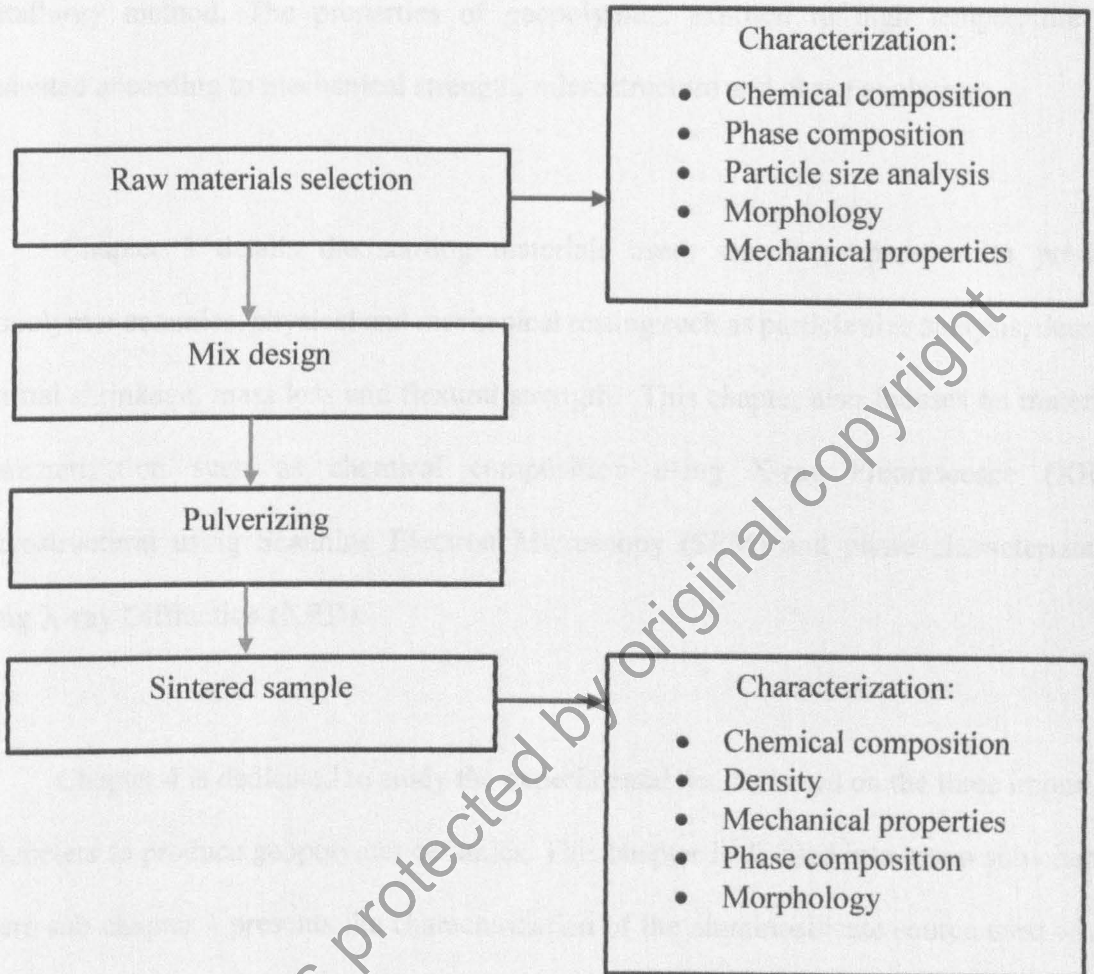

Figure 1.1: Details of the work flow for this research.

1.5 Organization of Thesis

This thesis is organized in five chapters. Following this introductory chapter, the other chapters are structured as follows:

Chapter 2 reviews the relevant literature on geopolymer and geopolymerization. Topics covered in this chapter include the historical development of geopolymer as an alternative binder and source material used for geopolymer synthesis. The main focus of this chapter highlighted the fabrication method of geopolymer ceramic by using powder metallurgy method. The properties of geopolymers exposed to high temperature are evaluated according to mechanical strength, microstructure and phase evolution.

Chapter 3 details the starting materials used, sample preparation to produce geopolymer ceramics, physical and mechanical testing such as particle size analysis, density, thermal shrinkage, mass loss and flexural strength. This chapter also focuses on materials characterization such as chemical composition using X-ray Fluorescence (XRF), microstructural using Scanning Electron Microscopy (SEM) and phase characterization using X-ray Diffraction (XRD).

Chapter 4 is dedicated to study the experimental results based on the three important parameters to produce geopolymer ceramics. This chapter is divided into seven sub-chapter where sub-chapter 1 presents the characterization of the aluminosilicate source used which is kaolin. Sub-chapter 2 discuss the mechanical properties and characterization of kaolin ceramic. Sub-chapter 3 to 5 discusses the effect of NaOH concentration, Na_2SiO_3/NaOH ratios and sintering temperatures on kaolin geopolymer ceramics, sub-chapter 6 and 7 discuss about correlation between parameters and comparison between control sample and kaolin geopolymer ceramic (KGC).

Chapter 5 comprises of a conclusion based on the obtained results and suggestions that can be applied for further and/or future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The research into geopolymers was led by the needs of new heat resistant materials after various catastrophic fires in France in 1970. Geopolymer is an inorganic polymeric material developed by Davidovits (1991). This breakthrough has replaced the dependency to high temperature techniques to produce materials which are ceramic-like in their properties and structures. This is because geopolymers yield amorphous to semi-crystalline structures and can polycondense like organic polymers at temperatures below than 100 °C (Davidovits, 1991). In addition, geopolymers are hard, inorganic, and stable up to 1250 °C and non-inflammable (Davidovits, 1994).

Research has been done on the development of geopolymers due to the wide potential application in many sectors includes construction engineering, thermal insulation of buildings and aeronautical engineering (Salahuddin et al., 2015). The current biggest contribution of geopolymers was in the construction industry by replacing cement in building materials and as binders for concretes (Atiş et al., 2015). Hence, geopolymer is environmental friendly materials by reducing carbon dioxide (CO_2) emission (Heikal et al., 2014). However, there was limited studies focusing on the high temperature application of geopolymers.

Recent technology has been focusing on widening the application of geopolymer by conversion to ceramics when heating. Hence, geopolymer acts as a precursor to ceramic forming. Though geopolymer is generally x-ray amorphous if cured at standard pressures and temperatures, it will convert to crystalline ceramic upon heating where the chemical composition in the geopolymer will went through series of reaction to transform into crystalline phase (He et al., 2013; Oh et al., 2010). Geopolymer can potentially be heated to form intricately shaped ceramics and ceramic composites (Bell et al., 2009b).

2.2 Geopolymer

Davidovits (1994) has defined geopolymers as mineral polymers resulting from geochemistry or geosynthesis where it is the science of manufacturing artificial rock at a temperature below 100 °C in order to obtain natural characteristics such as hardness, longevity and heat stability. According to Buchwald (2006) the prefix "geo" was to symbolize the constitutive relationship of the binders to geological materials such as natural minerals. The "-polymer" part refers to the composition of the geopolymers which is a three dimensional network of monomers consisting of aluminate and silicate tetrahedral (Kim et al., 2006; Weerdt, 2011).

Geopolymers are classed as inorganic polymers which can be produced by synthesizing pozzolanic compounds or aluminosilicate materials with highly alkaline solutions. Pozzolans can be defined as materials that contain mainly of SiO_2 and Al_2O_3 (Swanepoel & Strydom, 2002). Poly(sialates) was introduced as chemical designation for geopolymers based on silico-aluminates. According to Davidovits (2002), geopolymers