THE EFFECT OF SINTERING TEMPERATURE ON POTASSIUM FELDSPAR ADDITION INTO CLAYTAN PORCELAIN

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Dedicated with much love to my beloved mother Habibah Binti Pandak Leman, to my lovely husband, Mohd Azmi Bin Zulkifli, You are the love of my life, my strength and support. This thesis is also dedicated to my lovely sons Muhammad Izzat, Muhammad Ikhwan Zulhakim, Muhammad Danial Haikal, Muhammad Safwan Muaz and my daughters Nurin Irdina, Khairunnisa and Alya Insyirah . You are my inspirations.

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ABSTRACT

Porcelain is one of the most complex ceramic materials composed mainly of kaolin, quartz and feldspar. Its diverse applications include tableware, whiteware and insulators. This study was performed to investigate the effects of different sintering temperature on Claytan porcelain with the addition of 0wt%, 2wt%, 4wt%, 6wt%, 8wt% and 10wt% of potassium feldspar. The study was done using the slip casting. Slip added with potassium feldspar was poured into a plaster mold and then dried. The samples were sintered at temperature 800°C, 900°C, 1000°C and 1100°C with heating rate of 10°C/min and 1 hour holding time. The samples were characterised and analysed using mechanical testing, physical analysis and observation of the surface morphology by field scanning electron microscope (FESEM). The results show that the bulk density and modulus of rupture increased when the sintering temperature increased. This is because of the decrease in the percentage of apparent porosity. This result was consistent with the analysis of surface morphology. While an increase of more than 2wt% potassium feldspar would affects the physical and mechanical properties as proven from the observation of surface morphology. The result shows that the best state of physical and mechanical properties was when the sample is sintered at 1100°C with 2wt% of potassium feldspar. At this temperature and composition the value of the percentage of apparent porosity is 29.053%, bulk density 2.060g/cm^3 and the modulus of rupture is 17.352MPa.

ABSTRAK

Porselin adalah satu contoh bahan seramik yang komplek, mengandungi kaolin, kuartz dan feldspar. Ia digunakan secara meluas terutamanya dalam pembuatan pinggan mangkuk, tembikar putih dan insulator. Kajian ini telah dijalankan untuk mengkaji kesan suhu persinteran terhadap porselin Claytan yang telah ditambah potassium feldspar mengikut komposisi 0%, 2%, 4%, 6%, 8% dan 10%. Kajian ini menggunakan kaedah tuangan slip. Slip yang telah dicampur dengan potassium feldspar dituang ke dalam acuan plaster dan dikeringkan. Sampel telah disinter pada suhu yang berbeza iaitu 800^{o}C, 900^{o}C, 1000^{o}C dan 1100^{o}C dengan kadar pemanasan 10^{o}C/min serta direndam selama 1 jam. Sampel kemudiannya diuji dan dianalisis sifat mekanikal, fizikal dan pemerhatian ke atas morfologi permukaan dengan menggunakan mikroskop imbasan electron (FESEM). Hasil ujian telah menunjukkan bahawa nilai ketumpatan dan modulus kegagalan semakin meningkat apabila meningkatnya peratus keliangan. Hasil ujian ini adalah konsisten dengan hasil dari analisis morfologi ke atas permukaan sampel. Keputusan ujian telah menunjukkan bahawa sifat fizikal dan mekanikal sampel adalah optimum apabila mengalami suhu persinteran 1100^{o}C dengan penambahan potassium feldspar sebanyak 2%. Pada suhu dan komposisi ini nilai peratus keliangan adalah 29.053%, ketumpatan 2.060g/cm^3 dengan nilai modulus kegagalan 17.352MPa.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	-	American Society Testing manual Service
DTA	-	Differential thermal analysis
FESEM	-	Field emission scanning electron microscope
MOR	-	Modulus of rupture
TGA	-	Thermal gravimetric analysis

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Ceramics have been used for many thousand years. Nearly all tools and decorations were made from stone and ceramics. Its name is derived from the Greek "*keramos"* which means "pottery" (Kingery, 1960). Webster defines *ceramics* as "of or having to do with pottery" (Webster's Dictionary, 1988). Ceramics can be classified according to their properties and applications and that it is common to class them as traditional ceramics or advanced ceramics.

Traditional ceramics are usually based on clay, silica, mineral oxides and feldspar and people sometimes have a tendency to equate traditional ceramics with low technology. They are used in a variety of applications including porcelain, refractory and structural clay products (Carter, 2007).

Traditional ceramics are characterized by mostly silicate-based porous microstructures that are quite coarse, non-uniform, and multiphase. This ceramic is typically formed by mixing clays and feldspars, followed by forming either by slip casting or on a potter's wheel, firing in a flame kiln to sinter them, and finally glazing. The applications of traditional ceramics are quite common, from sanitary ware to fine china and porcelains to glass products (Barsoum, 2003).

Advanced ceramics are also referred to as engineering ceramics which are more superior in mechanical properties. The advanced ceramics is the materials that are well defined and their controlled properties are produced from nearly chemically and phase pure starting materials. The three categories of advanced ceramics can be classified as oxides ceramics, non-oxides ceramics and composite ceramics. Alumina and zirconia are examples of oxide ceramics. Carbides, borides, nitrides and silicates are non-oxide ceramics and ceramic based composite are the particulate reinforced and a combination of oxides and non-oxides (Carter, 2007).

Traditional clay-based ceramics have been used for over 25,000 years, while advanced ceramics have generally been developed within the last 100 years (Richerson & David, 2006). The main emphasis in this research is the traditional or clay based ceramics as ceramic porcelain lies in this category. As mentioned before, mineral silicates, such as clay and silica (such as quartz) are among the most abundant substances in nature, and are the ingredients for a variety of ceramic products.

Pottery and tableware are one of the oldest, but they are still one of the most important products today. These products are made from clay and other minerals such as silica and feldspar.

1.2 Problem Statement

The process of sintering is very important in order to prepare the ceramic body for the consolidation of particles under the temperatures below the melting point mostly by solid-state reactions. Sintering will form solid bonds between particles. Such bonding reduces the surface energy by reducing the free surface. From the sintering process, the grain boundaries are partially eliminated through grain growth and the pore volume is reduced, leading to a condensed mass. The temperature necessary to induce such bonding depends upon the characteristics of both starting materials and the particle size distribution (Richerson & David, 2006).

Regarding the body of ceramic whiteware, there are a number of studies using the low sintering temperature. For example, Kivitz *et al*. (2009) studied the reduction of the porcelain sintering temperature by using the preparation of the raw materials. They used common porcelain slurry consisting of kaolin clay 36.85wt%, feldspar 12.73wt%, quartz 17.42wt%, water 33wt % and an industrial commercial deflocculant that was conventionally batch prepared by the industry. The slurry was then ground in an agitator ball mill from d_{50} = 5.0µm to 0.9µm. They found that the sintering temperature can be decreased to about 180^{o}C after grinding the raw material (Kivitz et al., 2009).

Moreover Ito, (2008) reported that the stoneware body with a composition of 40wt% clay, 20wt% Indian feldspar, 20wt% nepheline syenite and 20wt% petalite can be sintered at 1100^{o}C (Ito, 2008).

The material studied in this work is Claytan porcelain. Typically porcelain that are frequently used for tableware have a tri-axial composition comprising 50% clay, 25% flux and 25% feldspar. As we know the sintering temperature is one of the most important processing variables in the manufacture of ceramic products including the product of porcelain tableware. In fact, in some cases, it defines the final product cost. To keep up its competitive capability and high quality, the porcelain industry needs new innovations which also require a change in the preparation of raw materials and sintering process. The purpose of this study is to decrease energy by the reduction of temperature during the sintering process. One way of reducing the sintering temperature is by using potassium feldspar as a flux.

At the same time, the effect of weight percentages of potassium feldspar as additive material to the physical and mechanical properties of the samples together with phase formations and morphology of the formed phases were studied. So, the main aim of this research is using potassium feldspar as an additive material for Claytan porcelain and analysing the mechanical properties in order to produce porcelain which satisfies the same level as required by the standards.

1.3 Objective of Study

The objectives of this research are:

i. To study the influence of different sintering temperature on Claytan porcelain with additive of potassium feldspar.
ii. To establish the optimum sintering temperature.
iii. To characterize the thermal analysis, structural, physical and mechanical properties of Claytan porcelain.

1.4 Research Scope

The scopes of this research are shown as follows:

i. The samples were sintered at temperature 800^{o}C, 900^{o}C, 1000^{o}C and 1100^{o}C with a sintering rate of 10^{o}C/minute with 1 hour holding time.
ii. Effect of different composition of potassium feldspar into the Claytan porcelain with different composition (0wt%, 2wt%, 4wt%, 6wt%, 8wt% and 10wt %) to the physical and mechanical properties.
iii. To analyze the structure and the physical properties of the study material by using:
    (a) Thermo gravimetric analysis method (TGA)
    (b) Linear shrinkage, density and porosity testing
    (c) Micro hardness vickers tester
    (d) 3 points bending test (MOR)
    (e) Field Emission Scanning Electron Microscopy method to determine the characteristics and morphology of the samples

1.5 Significant of Study

The significant of this study is to review the sintering effect on Claytan porcelain with the addition of potassium feldspar composition. The significant of the study is to have the best properties and to reduce the sintering temperature process of the Claytan porcelain. If this study can be proven, the sintering process of this ceramic material can save the energy and manufacturing costs of the ceramic products.

CHAPTER 2

LITERATURE REVIEW

2.1 Porcelain

Today, porcelain is produced in many countries and the most popular products are porcelain tableware and porcelain stoneware. Porcelain, glass, bricks and refractory materials are some examples of traditional ceramics (Wachtman *et al.,* 2009). By the ASTM definition, porcelain is a glazed or unglazed vitreous ceramic whiteware made by the porcelain process used for technical purposes to designating such products as electrical, chemical, mechanical, structural and thermal wares when they are vitreous.

Porcelain has a great variety of purposes in present day science, engineering and everyday life. This is because, as a technical material, porcelain possesses a number of valuable properties that are high in mechanical and electric strength, good chemical resistance and spalling resistance in the material made from commonly found crude mineral (Budnikov, 1964).

Porcelain or sometimes known as triaxial porcelain is the term used to describe vitrified whiteware, translucent in thin layers, impermeable to fluids, and manufactured from a fine mixture of clay such as kaolin, quartz and feldspar. Porcelain typically has a triaxial formulation comprising about 50% clay, 25% flux and 25% filler (Lee & Iqbal, 2001). Figure 2.1 shows a three component diagram of these ingredients for typical porcelain ceramic.

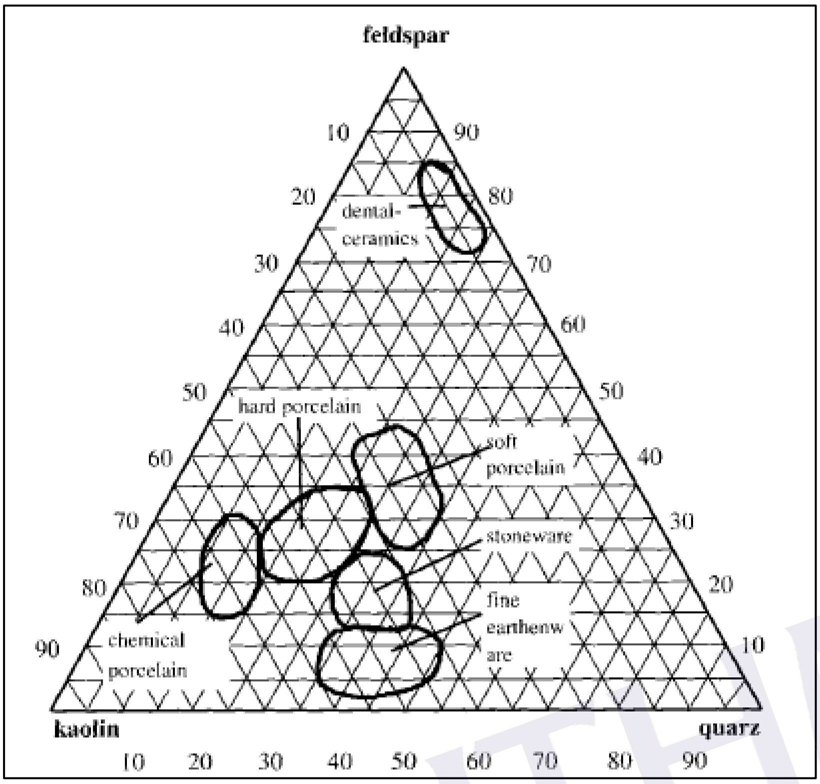

Figure 2.1: Typical Compositions of porcelain ceramic (Buchel, 1989)

The clay is the most important part among the formulation, which forms the body of porcelain. It provides green strength and plasticity during the porcelain forming stages. About half part of the porcelain body is composed of clay (Lee *et al*,. 2008).

Quartz and flint, are the most common fillers used for porcelain bodies, in which dissolution of silica in feldspathic glass is an essential part in its microstructural evolution. During the process of sintering, it melts and forms a glassy phase which provides the respective bonding strength and forms a dense structure. The filler materials usually have really high melting temperatures and are chemically resistant at commercial firing temperatures (below 1300°C). Quartz will help in reducing the tendency of the body to shrink, distort or warp when sintered at temperatures forming high quantity of viscous glass. Too little quartz can result in poor glaze fit, leading to problems of crazing, while too much will shatter or crack the body (Ryan, 1978).

Another important raw material for traditional ceramics is feldspar. According to Budnikov (1964), feldspar is actually the solvent of the two previous materials, based on their percentage ratios and the temperature range attained during product firing.

In whiteware bodies, the function of feldspars are used as fluxing agents to form a glassy phase at low temperatures and as a source of alkalies and alumina in glazes. The first glassy phase to form is due to a ternary eutectic. They improve the strength, toughness, and durability of the ceramic body (Kyonke, 2007).

There are two types of porcelain, the first one is hard porcelain and the second is soft porcelain. Hard porcelain contains less feldspar and more kaolin and is fired at higher temperatures than the mixtures used for soft porcelain. The properties of hard porcelain are suitable for making insulators and equipment for the chemical industry and is the best source of domestic ceramic. This is because, it exhibits high mechanical strength, good dielectric characteristics and high chemical resistance (Budnikov, 1964).

Soft porcelain, in contrast to hard porcelain contain more feldsfar, and therefore has more fusibles and has a lower sintering temperature (1300^{o}C–1350^{o}C) than is required for hard porcelain. It is fairly hard after fairing, and it is used to make a variety of household and decorative porcelain ware (Budnikov, 1964).

Various types of porcelain are obtained through the physical and chemical interaction of the argillaceous matter, quartz and feldspar at high temperatures. The phase composition and properties due to it depends on the kaolin and plastic clay, quartz and feldspar content in the porcelain mixture, on the chemical composition of these materials and degree of pulverization and also on the temperature and period of sintering (Budnikov, 1964).

A very important factor in the structure of porcelain is the presence of pores, which reduce the grade of the porcelain. The highest porosity (35 – 40%) occurs just before the sintering point. As the vitreous mixture fills the pores forms, the porosity is reduced and the density of the material is increased and there is a corresponding reduction in size (Richerson & David, 2006).

Total elimination of the pores is prevented by the gas enclosed within them, formed through physical and chemical interaction between certain components in the mixture at high temperatures. The high viscosity of feldspar glass makes it difficult for the gas bubbles to escape from the porcelain, which is why the sealed pores are formed (Richerson & David, 2006).

An increase in the amount of fusibles in the porcelain and a higher sintering temperature help to increase the amount of vitreous phase and help it to fill up the pores. However, sintering porcelain at temperatures above the norm for the given mixture results in the liberation of gas from the feldspar glass, bloating of the porcelain and a decline in quality. The pores reduce the mechanical and electric strength of porcelain, its chemical resistance and certain other valuable properties. Thus for critical parts the porosity should not exceed 0.1 – 0.3% (Richerson & David, 2006).

There are two ways of obtaining sufficient low viscosity glass to ensure a dense porcelain structure with minimum number of pores. This is done by increasing the amount of feldspar in the mixture and by prolonging the sintering period and increasing the sintering temperature.

2.1.1 Formation of porcelain

Figure 2.2 shows five stages of the phenomena occurring between the grains of kaolinite clay, quartz and feldspar which are the basic components of the porcelain mixture. Endothermal effect occurs within the temperature 500°C to 550°C, where this is the first stage of firing. Dehydration of the kaolin occurs in accordance with the following reaction (Budnikov, 1964):

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O \qquad (2.1)$$

Meta kaolinite decomposes into oxides at a temperature between 800°C to 900°C. At this stage, the initial shape of the kaolinite platelets are being preserved as the following reaction (Budnikov, 1964):

$$Al_2O_3.2SiO_2 \rightarrow \gamma.Al_2O_3 + 2SiO_2 \qquad (2.2)$$

Crystallization of γ-alumina occurs within the range of 950°C-1000°C accompanied by a considerable exothermal effect. During the next stage of firing, above 1000°C, a stable form of the alumina silicate is formed at this high temperature and atmospheric pressure, called the mullite. The mullite formation can start at 980^{o}C and as the temperature is increasing more mullite phase is formed. The formation of mullite and free silica in the form of cristoballite are as mentioned below (Budnikov, 1964):

$$3Al_2O_3+6SiO_2 \rightarrow 3Al_2O_3.2SiO_2 + 4SiO_2 \quad (2.3)$$

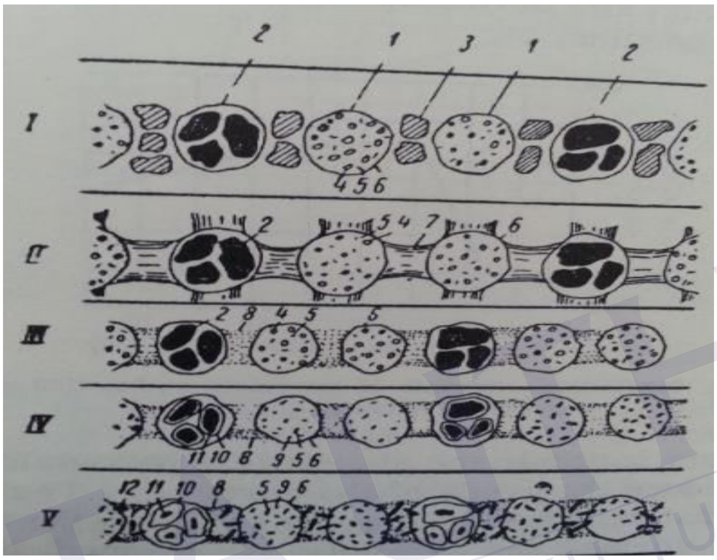

Figure 2.2: Formation of porcelain (Budnikov, 1964)

2.1.2 Potassium Feldspar

Potash feldspar ($K_2O.Al_2O_3.6SiO_2$) are the most extensively used fluxes for porcelain manufacturing, followed by soda feldspar ($Na_2O.Al_2O_3.6SiO_2$) and lime feldspar ($CaO.Al_2O_3.2SiO_2$). The theoretical chemical compositions for three feldspar are shown in Table 2.1.

Table 2.1: Theoretical compositions of pure feldspar (Kyonke, 2007)

Type of feldspar	**K_2O**	**Na_2O**	**CaO**	**Al_2O_2**	**SiO_2**
Potassium feldspar ($K_2O.Al_2O_2.6SiO_2$)	16.9			18.3	64.8
Soda Feldspar ($Na_2O.Al_2O_3.6SiO_2$)		11.8		19.4	68.8
Lime Feldspar ($CaO.Al_2O_3.2SiO_2$)			20.2	36.6	43.2

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