EFFECT OF NIOBIUM OXIDE (Nb_2O_5) ADDITION TO THE PHYSICAL AND MECHANICAL PROPERTIES OF COLD ISOSTATIC PRESS ZIRCONIA TOUGHENED ALUMINA (ZTA)

NURUL KHAIRUNNISA BINTI SU

UNIVERSITI MALAYSIA PERLIS

2018

Effect of Niobium Oxide (Nb_2O_5) Addition to the Physical and Mechanical Properties of Cold Isostatic Press Zirconia Toughened Alumina (ZTA)

by

Nurul Khairunnisa Binti Su
1530411928

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

School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

2018

THESIS DECLARATION FORM

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name	: Nurul Khairunnisa Binti Su
Date of birth	: 18 November 1984
Title	: Effect of Niobium Oxide (Nb_2O_5) addition to the Physical and Mechanical Properties of Cold Isostatic Press Zirconia Toughened Alumina (ZTA)
Academic Session	: 2015/2016

I hereby declare that this thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as :

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act1972)

☐ **RESTICTED** (Contains restricted information as specified by the organization where research was done)

☐ **OPEN ACCESS** I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of _____ years, if so requested above).

Certified by:

______________________	______________________
SIGNATURE	**SIGNATURE OF SUPERVISOR**
841118-09-5102	DR. BANJURAIZAH BINTI JOHAR
(NEW IC NO. / PASSPORT NO.)	**NAME OF SUPERVISOR**
Date :______________	Date : ______________

ACKNOWLEDGEMENTS

Praise be to Allah, the Almighty and Merciful, who has given me the strength to finish this thesis. I would like to thanks for those who help me in writing this thesis. The first sincere gratitude goes to my main supervisor, Dr. Banjuraizah binti Johar, for the understanding, generous guidance and supports, from the beginning until the completion of my research. I would like to express my great appreciation to Dr. Muhammad Asri bin Idris for the contribution on the co-supervision and valuable suggestions for this research and thesis. I would like also to express my gratitude to Prof. Dr. Hj. Zainal Arifin bin Hj. Ahmad (USM), as co-supervisor, providing me with outstanding research facilities at Universiti Sains Malaysia (USM) in order to fulfil the laboratory work needed for this research. I would like to thanks to dean, Dr. Mohd Firdaus bin Omar, deputy deans, Dr. Muhammad Firdaus bin Mohd Nazeri, postgraduate program chairman, Dr. Azlin Fazlina binti Osman, Assoc. Prof. Dr. Khairel Rafezi bin Ahmad, lecturers and all staffs of the School of Materials Engineering, Universiti Malaysia Perlis (UNIMAP), for their kind assistant and supports until completed my research. I gratefully acknowledge Ministry of Education Malaysia for the scholarship of Hadiah Latihan Persekutuan (HLP) throughout my study. I would like to thanks to Mr. Mohd.Shahid bin Abd. Jalal, Mr. Khairi bin Khalid, Mr Zaini bin Saari, Mr. Mokhtar bin Mohamad, Mr. Farid bin Abd. Rahim, and Mr. Sharul Ami bin Zainal Abidin for their experimental and technical assistant. I would also like to express my thanks to my colleagues friends; Kok Eing Kuan, Tinesha a/p Selvaraj, Siti Rohani binti Zainudin and Siti Khalijah binti Kamarudin for helping me throughout my study by sharing knowledge in research work and to one and all, directly or indirectly have helping me in this research. Special thanks to my beloved husband, Nik Akmar bin Rejab for the supports, understanding and encouraging me throughout my study. I am extremely grateful to my sons, Alauddin Muqarrobin and Ashman Mustaqim that was so well behaved and cooperative during my study, thus given me the strength in my study. The appreciation for both of my parents, Su bin Musa and Rosiah binti Ahmad. With their helps, supports and encouragement had given me the strength in completed my study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al_2O_3	Alumina
c/a	Tetragonality
CIP	Cold Isostatic Pressing
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
HIP	Hot Isostatic Pressing
HV	Vickers Hardness
ICSD	Inorganic Crystal Structure Database
Kgf	Kilogram-force
MPa	Mega Pascal
m-ZrO_2	Monoclinic Zirconia
Nb_2O_5	Niobium oxide
$Nb_2Zr_6O_{17}$	Diniobium hexazirconium
PSZ	Partially Stabilised Zirconia
SEM	Scanning Electron Microscopy
t-ZrO_2	Tetragonal Zirconia
wt.%	Weight percentage
XRD	X-ray diffraction
Y_2O_3	Yttrium oxide
YSZ	Yttria Stabilised Zirconia
ZrO_2	Zirconia
ZTA	Zirconia Toughened Alumina
ZTA-Nb_2O_5	Zirconia Toughened Alumina with the addition of niobium oxide

LIST OF SYMBOLS

a	Half of the indentation diagonal length
a	Lattice parameter a
c	Lattice parameter c
d_{50}	Mean diameter
E	Modulus Young
GOF	Good of Fitness
HV	Vickers hardness
K_{1c}	Fracture toughness
L	Length of the radiant crack
l_i	Initial length of sample
l_f	Final length of sample
(c)	Cubic phase
(t)	Tetragonal phase
(m)	Monoclinic phase
ρ_b	Bulk density
R_{exp}	R expected
R_p	R Profile
R_{wp}	Weight R Profile

Kesan Penambahan Niobium Oksida (Nb_2O_5) Terhadap Sifat Fizikal dan Mekanikal Alumina Diperkuat Zirkonia Distabilkan Yttria (ZTA) melalui Kaedah Penekanan Isostatik Sejuk

ABSTRAK

Kesan penambahan niobium oksida (Nb_2O_5) terhadap sifat fizikal dan mekanikal alumina diperkuat zirkonia distabilkan yttria (ZTA) melalui kaedah penekanan isostatic sejuk telah dikaji. Pelbagai komposisi Nb_2O_5 (0 - 7 wt.%) ditambah ke dalam ZTA secara berasingan melalui kaedah pensinteran keadaan pepejal. Pengaruh Nb_2O_5 terhadap ZTA dikaji melalui sifat-sifat struktur, mikrostruktur dan mekanikal bahan seramik ZTA. Analisis XRD mengenal pasti kehadiran fasa t-ZrO_2, fasa m-ZrO_2 dan fasa $Nb_2Zr_6O_{17}$ dalam sistem ini. Kehadiran fasa $Nb_2Zr_6O_{17}$ memberikan penurunan nilai pada sifat seramik ZTA, yang berkaitan dengan lebihan had keterlarutan Nb_2O_5 di dalam seramik ZTA. Nilai optimum telah dicapai bagi 1 wt.% Nb_2O_5, yang memberikan nilai tertinggi untuk kekerasan Vickers (1840 HV), keliatan patah (8.60 $MPa.m^{1/2}$) dan kekuatan lenturan (351 MPa). Nilai keliangan yang rendah menyebabkan berlakunya peningkatan pada sifat-sifat mekanikal bahan. Jasad yang padat telah diperolehi melalui kaedah CIP dengan ketumpatan relatif mencapai 99.8% daripada ketumpatan teori. Pesongan retak yang terhasil dari kaedah lekukan menyebabkan peningkatan pada keliatan patah. Transformasi fasa ($t \rightarrow m$) yang berlaku di dalam sistem ini juga memberikan peningkatan pada nilai keliatan patah dan kekuatan lenturan. Nilai yang diperoleh menunjukkan bahawa Nb_2O_5 didapati telah meningkatkan sifat-sifat fizikal dan mekanikal seramik ZTA. Seterusnya, menghasilkan seramik yang mempunyai sifat kekuatan dan keliatan yang tinggi.

Effect of Niobium Oxide (Nb_2O_5) Addition to the Physical and Mechanical Properties of Cold Isostatic Press Zirconia Toughened Alumina (ZTA)

ABSTRACT

Effect of niobium oxide (Nb_2O_5) addition to the physical and mechanical properties of cold isostatic press zirconia toughened alumina (ZTA) was investigated. Various amount of Nb_2O_5 (0 - 7 wt.%) were added into ZTA separately through solid state method. The influences of Nb_2O_5 addition were investigated on the structural, microstructural and mechanical properties of ZTA ceramics. XRD analysis identified the presence of t-ZrO_2, m-ZrO_2 and $Nb_2Zr_6O_{17}$ phase in this system. The presence of $Nb_2Zr_6O_{17}$ phase found to deteriorate the properties of ZTA ceramic, which is related to the solubility limit of Nb_2O_5. The optimum value was achieve at 1 wt.% Nb_2O_5, which gives the highest value for Vickers hardness (1840 HV), fracture toughness (8.60 MPa.m$^{1/2}$) and flexural strength (351 MPa). The lower porosity results in the enhancement of the mechanical properties. Dense body was obtained via CIP method with the relative density achieve 99.8% to the theoretical density. The crack associated from indentation technique related with the increasing of fracture toughness value due to the presence of crack deflection. The phase transformation (t $\rightarrow$ m) also occurs in this system and resulted in improvement for fracture toughness and flexural strength. The obtained values indicated that Nb_2O_5 found to improve the physical and mechanical properties of ZTA ceramic. Thus, the high strength and toughness of ZTA ceramic can be produced.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Numerous study have been carried out in developing engineering ceramic and composites with high mechanical properties correlated with strength and fracture toughness (Calambás Pulgarin & Albano, 2014; Fornabaio et al., 2015; Rejab et al., 2013b; Rittidech et al., 2013; Y. Zhang et al., 2013). Nowadays, Al_2O_3 and ZrO_2 ceramics has been extensively used in industrial and biomedical field. These Al_2O_3-ZrO_2 ceramic produced zirconia toughened alumina (ZTA), where ZrO_2 particles are embedded into alumina matrix as a second phase. To date, ZTA composites application can be found in numerous applications such as bearings, cutting tools or in orthopedic and dental implants for biomaterials field. The requirement for this application is possible with the materials that has high melting points, chemical inertness, high hardness and has the ability to maintain the mechanical strength at higher temperature (Kern et al., 2015).

It has been established that ZrO_2 ceramics can display enhanced strength and toughness through transformation toughening mechanism. This mechanism is based on the polymorphic transformation of tetragonal ZrO_2 phase into monoclinic ZrO_2 phase (t → m) during cooling from sintering temperature to room temperature (Benavente et al., 2014).

ZrO_2 exists in three polymorphic forms, known as monoclinic (m), tetragonal (t) and cubic (c) phase, depending on temperature and chemistry. The room temperature phase is monoclinic which is stable below 1170^oC. Between 1170^oC and 2370^oC, ZrO_2 is in tetragonal form while over 2370^oC ZrO_2 in the form of cubic. Pure ZrO_2 transformation from the t → m phase takes place during cooling after material sintering which associated with a volume expansion of 3 - 5% (Hjerppe, 2010). ZrO_2 can be retained in tetragonal phase with the introduction of stabilizing oxides, such as yttria (Y_2O_3), cerium oxide (CeO_2), calcium oxide (CaO), magnesium oxide (MgO) and most rare earth oxides (Rittidech & Suekwamsue, 2015; Tekeli, 2005).

In addition, the compaction method used in producing ceramic with excellent properties also being considered. There are several method used including uniaxial pressing, isostatic pressing such as cold isostatic pressing (CIP) and hot isostatic pressing (HIP) or hot pressing. Most of the ceramic was prepared by uniaxial pressing compaction. However, the used of cold isostatic pressing method proved the improvement in the properties of the ceramics compared to uniaxial pressing method. CIP improved the densification with more uniform density distribution, which resulted in an improvement of the mechanical properties for the ceramics (Oberacker, 2012).

For this work, different amount of Nb_2O_5 (0 - 7 wt.%) are used as an addition to the ZTA ceramics via cold isostatic pressing (CIP) method in order to develop ZTA ceramics with excellent properties.

1.2 Problem Statement

Oxide additives play a significant role to improve ZTA properties through transformation toughening mechanism. More attention had been given by previous researcher using trivalent oxide additive such as Cr_2O_3, Ce_2O_3, Y_2O_3 and $CaCO_3$ which introduced as stabilizer to enhance the mechanical properties of ZTA ceramics through the transformation of tetragonal to monoclinic (t $\rightarrow$ m) in ZrO_2 structure which attributed to the crack shielding (Casellas et al., 2001). Besides trivalent oxide, there was also work done using pentavalent oxides as an additive to improve the properties of ZTA ceramics. Contrary to trivalent oxide, pentavalent oxide was also found to be dissolved in the ZrO_2 lattice and influenced the structure and properties of ZrO_2 (Almeida et al., 2007). The study of various oxide additives to ZTA for improving the physical and mechanical properties has been accomplished by many researchers through manipulating the additive contents depends on the applications. Hassan et al. (2015) added different amount of Nb_2O_5 (0.2 - 0.6 vol%) into ZTA, pressed using uniaxial pressing method and further sintered at 1650^{o}C for 1 hour soaking time. They found that by increasing Nb_2O_5 content, the physical and mechanical properties of ZTA could be improved with the maximum value of Vickers hardness, fracture toughness and flexural strength were 1792 HV, 6.19 MPa.m$^{1/2}$ and 298 MPa for 0.6 vol% Nb_2O_5 addition, respectively.

However, there are many factors can enhanced the hardness as well as the mechanical properties of the ceramics for example by increasing the compactability of the green body such as by using different pressing method, modified the particle characteristics, and the used of additive (binder and lubricant). A number of different approaches such as uniaxial press, cold isostatic pressing (CIP) or hot isostatic pressing (HIP) commonly used as compaction method. Among the powder compaction method, CIP or HIP is expected to provide parts with high density (Papitha et al., 2013). Due to the relatively expensive operation of HIP, CIP is considered for achieving the high density sintered body. CIP has the ability in producing homogenous and high green body of ceramics by reduced the directionality (Ng et al.,1997). This result in reduction of pores that existed in the ceramics, increased the densification, and thus also increased the mechanical properties. Galusek et al., (1999) proved that CIP improved the physical properties (density and porosity) and mechanical properties (hardness, fracture toughness and bending strength) of ceramics. CIP promotes the sintering, improving the particle packing and reorganizing the microstructure which normally takes place during the initial sintering stage, which can be attributed almost exclusively to elimination of defects and lowering the porosity (Akimov et al., 1997; Galusek et al., 1999).

Hence, an effort has been done in this recent work to improve the ZTA ceramics but using the CIP method and varies the Nb_2O_5 content added into ZTA system.

1.3 Objectives of the Study

The objectives of this study are:

i) To quantify phase present in ZTA added with different amount of Nb_2O_5.
ii) To identify the effect of Nb_2O_5 addition on morphology of ZTA ceramic by using cold isostatic pressing (CIP) method.
iii) To determine the influence of Nb_2O_5 addition on the physical and mechanical properties of ZTA ceramic by using cold isostatic pressing (CIP) method.

1.4 Scope of the Study

For this work, samples with a ratio of 80:20 for Al_2O_3 and 5YSZ were prepared with different amount of Nb_2O_5 addition (0, 0.1, 0.3, 0.5, 0.7, 1, 3, 5, and 7 wt.%). The mix powders were then being compacted to produce the green body through uniaxially pressed (10 MPa) and followed by cold isostatic pressing (150 MPa). The green body eventually sintered at 1600^{o}C for 4 hours. The bulk density and porosity percentage values were obtained by Archimedes principle. Vickers hardness (HV) and fracture toughness (K_{Ic}) were specified by Vickers indentation technique with a 30 kgf load. The sintered samples were indent for 10 times and the average value was taken. Fracture toughness was calculated by measuring the length of propagated cracks (c and a) at the diagonal of the pyramid shape. The measured of flexural strength was done in a three-point bending test using a universal testing machine by measuring 10 samples for each data point. Scanning Electron Microscopy (SEM) was employed to analyses the samples microstructure. The sintered bodies were thermally etched for 1 hour at 1550^{o}C before microstructure observation using Scanning Electron Microscopy (SEM). The identification of phases and quantitative analysis was performed by PANalytical X'pert HighScore Plus software used with the files of 'Inorganic Crystal Structure Database' (ICSD). For comparison between CIP and uniaxial sample, 1 wt.% sample was chosen and uniaxially pressed at 10 MPa. The green body then was sintered at 1600^{o}C for 4 hours and followed as CIP sample for determining the physical (bulk density and porosity) and mechanical properties (Vickers hardness, fracture toughness and flexural strength).

CHAPTER 2

LITERATURE REVIEW

The literature review is divided into eight major sections. Section 2.1 to 2.5 provides background information on the Al_2O_3, ZrO_2, yttria as stabilizer for zirconia, zirconia toughened alumina (ZTA), and niobium oxide as additives to the ceramics. The transformation toughening mechanisms of ZrO_2 toughened Al_2O_3 ceramics is discussed in Section 2.6. Sections 2.7 review the fabrication works and characterization of the ZTA ceramics. Meanwhile section 2.8 reviews about Rietveld refinement. This chapter discussed the background information to assist for understanding the aims and results for this research. It also reviews recent reports by other researchers with which these results can be compared.

2.1 Alumina (Al_2O_3) Ceramics

Al_2O_3 is a common name given to aluminum oxide (Al_2O_3) which produced from bauxite via Bayer process. Al_2O_3 powders were obtained through their transition temperatures during the heat treatment process. Figure 2.1 shows transition Al_2O_3 during the heat treatment processes. Al_2O_3 existed in several crystalline phase denoted as alpha (α), chi (χ) , eta (η), delta (δ), kappa (κ), theta (θ), and gamma (γ). The most stable form compound produced from the heat treatment was known as α-Al_2O_3. An example of α-Al_2O_3 is Corundum/sapphire (Shirai et al., 2009). α-Al_2O_3 has the crystal structure that organized in a sequence of ABABAB… with O^{2-} anions. Al_2O_3 arrange with Al^{3+} cations in hexagonal close packed and occupied two-thirds of the octahedral interstices as illustrated in Figure 2.2 (Smallman et al., 2007).

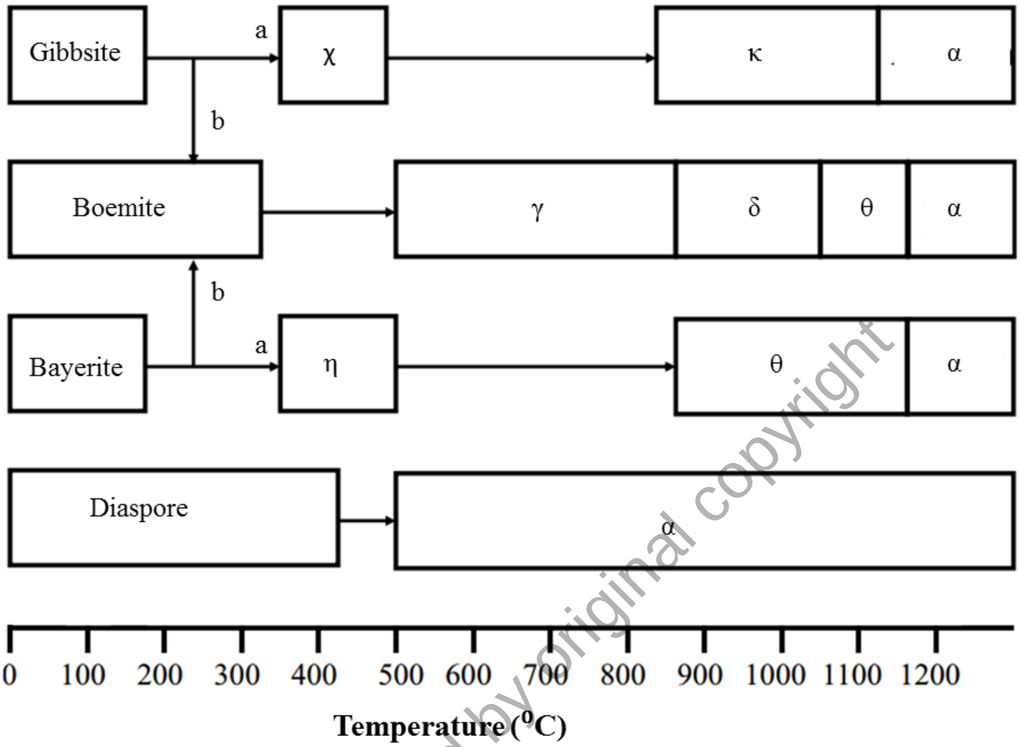

Figure 2.1: Structure transformation of Al_2O_3 and aluminum hydroxides (Shirai et al., 2009)

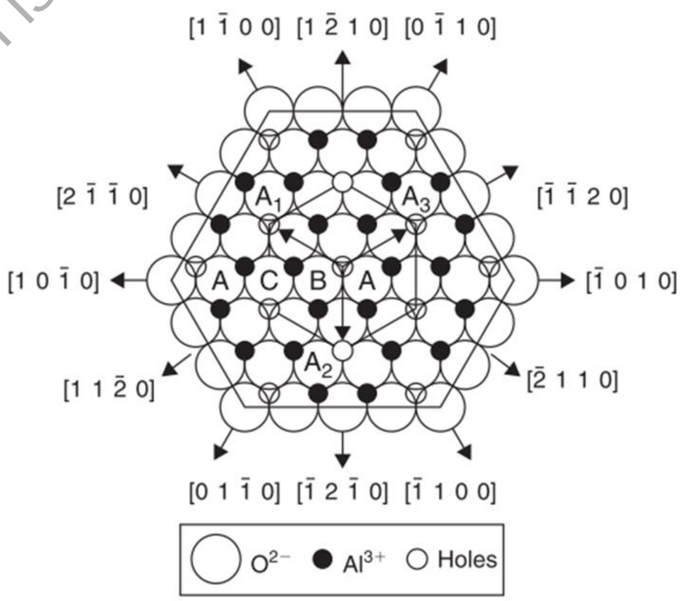

Figure 2.2: Structure of α- Al_2O_3 (corundum) viewed perpendicular to the (0001) basal plane (Smallman et al., 2007)

Al_2O_3 are extensively used as an engineering ceramic due to its excellent in mechanical properties, extremely resistance to wear and corrosion, high hardness, chemical stability behavior, and relatively cheap technology of production (Maiti & Sil, 2011; Szutkowska, 2012). Al_2O_3 has high melting point, which is above 2000°C and extensively used in structural applications such as in aerospace, motor and biomedical fields (Cesari et al., 2006). However, the brittleness of pure Al_2O_3 limits its potential applications (Tuan et al., 2008; Zhang et al., 2008). Table 2.1 and Table 2.2 listed the mechanical and thermal properties of Al_2O_3 with 99.7% purity.

Table 2.1: Mechanical properties of Al_2O_3 (Davis, 2010)

Properties	Values
Density (g/cm^3)	3.96
Elastic modulus (GPa)	375
Flexural strength (MPa)	410
Vickers hardness (HV)	1900
Fracture toughness (MPa.m$^{1/2}$)	4.0 - 5.0

Table 2.2: Thermal properties of Al_2O_3 (Davis, 2010)

Properties	Temperature Condition	Value
Maximum working temperature (ºC)	-	1700
Coef. thermal expansion (10^{-6}/ºC)	25 - 300ºC	7.8
Coef. thermal expansion (10^{-6}/ºC)	25 - 1000ºC	8.1
Thermal conductivity (W/mK)	20ºC	28

Due to the brittleness behaviour of Al_2O_3, significant improvements have been done for enhanced the mechanical properties of Al_2O_3. The brittleness behaviour of Al_2O_3 is characterized by its low fracture toughness (Szutkowska, 2012). The low fracture toughness was associates with the dislocation motion in the material which is in ionic or covalent bonds.