SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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EFFECT OF La_2O_3 ADDITION ON THE HARDNESS AND INDENTATION FRACTURE RESISTANCE OF ZTA-CeO_2-La_2O_3 CERAMICS

By

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DECLARATION

I hereby declare that I carried out the work reported in this report in the School Of Materials And Mineral Resources Engineering, University Sains Malaysia, under the supervision of Professor Dr. Hj. Zainal Arifin Bin Ahmad. I solemnly declare that to the best of my knowledge, no part of this report has been submitted here or elsewhere in a previous application for award of a degree. All sources of knowledge used have been duly acknowledged.

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LIST OF SYMBOLS

a	Half of the indentation diagonal length
a	Lattice parameter a
c	Lattice parameter c
d_{50}	Mean diameter
E	Young's Modulus
HV	Vickers hardness
K_{IC}	Indentation fracture resistance
K_{IFR}	Indentation fracture resistance
1	Length of the radiant crack
D_i	Initial length of sample
D_f	Final length of sample
(t)	Tetragonal phase
(m)	Monoclinic phase
ρ_b	Bulk density
wt.%	Weight percentage

LIST OF ABBREVATIONS

ASTM	American Standard for Testing Materials
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field Emission Scanning Electron Microscope
ICDD	International Centre for Diffraction Data
MOR	Modulus of Rupture
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction
YSZ	Yttria stabilized zirconia
ZTA	Zirconia toughened alumina

KESAN PENAMBAHAN La_2O_3 KEPADA KEKERASAN DAN RINTANGAN LEKUKAN PATAH KEPADA SERAMIK ZTA-CeO_2-La_2O_3

ABSTRAK

Kesan penambahan La_2O_3 kepada seramik alumina diperkuat zirkonia telah dikaji. CeO_2 telah ditambah di dalam sistem ZTA-CeO_2 yang bertindak sebagai bahan penambahan sinteran. Komposisi ZTA-CeO_2 telah dicampur sebati dengan peratusan berat La_2O_3 yang berbeza iaitu daripada 0.1 % berat sehingga 10 % berat. Bahan untuk setiap komposisi yang berbeza telah dicampur, dikeringkan selama 24 jam di dalam ketuhar pada suhu 100 °C. Campuran ini kemudiannya dimampat menggunakan pemampat hidraulik dalam acuan silinder pada tekanan 10 MPa membentuk sampel pelet. Seterusnya, sampel ZTA ini disinter pada 1600 °C dengan masa rendaman selama 4 jam di dalam relau elektrik yang bertekanan normal. Setiap sampel akan diuji dengan lekukan Vickers dengan daya 30 kgf bersamaan dengan 294 N. Lekukan Vickers ini bertujuan untuk mengukur nilai kekerasan Vickers dan rintangan lekukan patah bagi setiap sampel. Melalui pengoptimunan yang dilakukan sampel seramik ZTA-CeO_2-La_2O_3 dengan penambahan La_2O_3 sebanyak 0.85 % berat menunjukkan keputusan kekerasan Vickers yang tertinggi dengan catatan 1760.28 HV. Sampel seramik ZTA dengan penambahan La_2O_3 sebanyak 0.7 % berat menunjukkan keputusan rintangan lekukan patah yang tertinggi dengan catatan 8.28 $MPa.m^{1/2}$. Berdasarkan keputusan SEM, mikrostruktur jumlah butiran yang berbentuk rod menunjukkan peningkatan apabila peratus berat La_2O_3 yang ditambah di dalam sistem ZTA-CeO_2 meningkat. Kehadiran fasa sekunder butiran memanjang yang terbentuk itu dikenal pasti sebagai $LaAl_{11}O_{18}$. Fasa sekunder ini memainkan peranan penting dalam meningkatkan nilai kekerasan.

EFFECT OF La_2O_3 ADDITION ON THE HARDNESS AND INDENTATION FRACTURE RESISTANCE OF ZTA-CeO_2-La_2O_3 CERAMICS

ABSTRACT

The effect of La_2O_3 addition to zirconia toughened alumina (ZTA) ceramics has been studied. CeO_2 has been added in the ZTA system which acts as sintering additive. ZTA-CeO_2 composition mixed with La_2O_3 weight percentage from 0.1 wt.% by weight to 10 wt.% . The compositions for each type of composition have been mixed, dried for 24 hours in the oven at 100 °C. This mixture is then compressed using hydraulic compressor in the mold cylinder at 10 MPa to form sample pellets. Next, this ZTA sample is sintered at 1600 °C with 4 hours soaking in a pressureless sintering furnace. Each of the sample was tested with a Vickers indentation of 30 kgf equivalent to 294 N. The Vickers indentation is intended to measure the hardness of the Vickers value and indentation fracture resistance for each sample. From the optimisation, ceramic sample ZTA-CeO_2 with 0.85 wt.% La_2O_3 addition showed the highest Vickers hardness result with 1760.28 HV. ZTA ceramic samples with 1 wt.% addition of La_2O_3 showed the highest indentation fracture resistance results with 8.28 K_{IFR}. Based on the SEM results, microstructure showed that the amount of the grain is increase with the increase of weight percentage of La_2O_3 addition in the ZTA system. The presence of the secondary phase of the elongated rod-like grains formed was known as $LaAl_{11}O_{18.}$ This secondary phase plays an important role in increasing the value of hardness.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In ZTA ceramics, Al_2O_3 as the matrix and ZrO_2 embedded as reinforcement. As the reinforcement, an enhancement can be made by the two states of ZrO_2 that are commonly used in ZTA ceramics, either unstabilised or stabilised. Unstabilised ZrO_2 refer to the pure ZrO_2 without the presence of any stabilizer content which is not very useful as a structural materials. Meanwhile, stabilized ZrO_2 refer to the ZrO_2 with the presence of additives which acts as phase-stabilisers such Y_2O_3, MgO, and CeO_2. These oxides are very useful in its stabilized state. The role of these stabilizer is to retain the high-temperature phase, either monoclinic, tetragonal or cubic, at room temperature, which gives ZrO_2 its desirable properties as an engineering ceramic.

The presence of stabilizer can cause the tetragonal phase to convert to monoclinic phase, with the associated volume expansion. This phase transformation have a unique ability to stop the growth of cracks and enhancing the fracture toughness. This mechanism is known as transformation toughening, and significantly extends the reliability and lifetime of ZTA ceramics. The transformation toughening mechanisms of ZTA is mainly provided a combination of stress induced phase transformation (tetragonal to monoclinic zirconia) microcracks as well as crack deflection (Azhar et al., 2010).

In spite the utilization of stabilizer, the occurrence of cracks still not completely avoidable. In consequence, the ZTA cutting inserts are prematurely fail by chipping during high speed machining since the metal cutting process is one of the most severe applications of ceramics materials. The cutting edge and faces of an insert are exposed to high stress and elevated temperatures, as well as to thermal shock, especially in an intermittent cutting process. The advantages of using ZTA as cutting inserts material is the possibility of a spontaneous transformation from the tetragonal to the monoclinic phase.

The main influences of the t-ZrO_2 to m-ZrO_2 spontaneous transformation are the grain size, stabilizer content and distribution, the composition of the ZrO_2 as secondary phase and residual stresses resulting from the differences thermal expansion between the phases (Basu et al., 2004). The rate of spontaneous transformation could be increased with the presence of bigger grain size and difference between the thermal expansions of the phases. To meet these requirements, the new materials were developed by adding more than one additive or stabilizer in ZTA ceramics which is known in literature review that prevent the low temperature degradation, while retaining a relative high fracture toughness.

Reviews of La_2O_3 and CeO_2 has attracted this work to be carried out as relatively good and promising candidates to be added as stabilizer in ZTA ceramics. In addition, their ability as stabilizer through transformation toughening mechanisms and sintering aid of Al_2O_3 by the prevention of abnormal grain growth at the final stage of densification process which leads to superior properties ceramics (Wu et al., 2001). Therefore, in this research, with a detail assessments of suitability and properties effect of CeO_2 and La_2O_3 in ZTA ceramics in terms of toughening improvement is carried out.

1.2 Problem Statement

Many compositional developments have been made to improve the mechanical properties and controlled microstructure of ZTA. The utilization of sintering additives such as Cr_2O_3, NiO, TiO_2 and MgO was selected by researchers because these additives enable the achievement of fine grain size and high density at low sintering temperatures. Azhar et al. (2010) confirmed that, the mechanical properties of ZTA, such as its fracture toughness, can be improved with an accurate and efficient dosage of partially stabilized tetragonal ZrO_2 addition with definitely sized particles.

However, there are only scarce reports about the effects of La_2O_3 additions on the phases, microstructure and mechanical properties of ZTA. Therefore, in this study, we examine the effects of different La_2O_3 addition (0.1 wt.%-10 wt.%) on the phases, microstructure, and mechanical properties of ZTA systems. The phases and microstructure of the samples were observed using XRD and SEM. The mechanical properties, such as fracture toughness and Vickers hardness, were measured to determine the potential of the ZTA-CeO_2-La_2O_3 compositions.

1.3 Research Objectives

a) To compare the influence of different weight percentages of La_2O_3 to the indentation fracture resistance and microstructural characteristics

b) To optimise the addition of La_2O_3 that provide optimum properties and microstructure of the ZTA ceramics

1.4 Project Approach

ZTA-5 wt.% CeO_2 ceramic were fabricated with 9 different La_2O_3 wt.% addition. 5 wt.% of CeO_2 is used because it is the optimum wt.% addition that provide the highest fracture toughness and hardness as reported by Rejab et al. (2013a). The changes of mechanical and microstructural were examined in order to find the best composition. The raw materials were weighed, where each composition must followed the parameter given respectively. The ZTA consists of 80 wt.% of Al_2O_3 and 20 wt.% of ZrO_2. The amount of CeO_2 added is 5 wt.% for all compositions. The addition of La_2O_3 were varied from 0.1 wt.% to 10 wt.%. Each composition undergoing mixing to mix them homogeneously. Then, the compositions were dried for 24 hours. Dried compositions were crushed using agate mortar. The composition in form of powder. The powder was uniaxially compressed with 10 MPa load into pellet samples with dimension of 5 cm length and 1 cm width. The samples were sintered at 1600°C for 4 hours soaking time. Then, the properties of sintered body were examined. The properties are include porosity, density, indentation fracture resistance, hardness, microstructure and XRD analysis. Microstructure observation was done to investigate the grain structure of the ceramic. Furthermore, XRD analysis was carried out to identify the different phases exist in the ceramic.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The contents of this chapter are generally include the research gap in Section 2.2. Some previous research papers are cited from the literature as the bench mark to complete the aim of this current study. In the Section 2.3, briefly explained the systhesis process of this engineering ceramic. Alumina was explained as the most suitable and favorable ceramic material that suit the high speed cutting tools application. Nevertheless, alumina though have catastrophic failure as the indentation fracture resistance of alumina is not suitable for extreme environment of these application and yet alumina matrix need to be doped by zirconia as reinforcement within it for toughening improvement purpose. In Section 2.4, the toughening mechanism is discussed. These transformation is induced due to the phase transformation of zirconia from tetragonal to monoclinic phase when the temperature drop. Formation of yttria stabilized zirconia (YSZ) due to the retaining tetragonal phase of zirconia at high temperature is explained in Section 2.5. In Section 2.6, the introduction of YSZ in the alumina matrix gives result of zirconia toughened alumina which the indentation fracture resistance of alumina is improve by addition of stabilized zirconia and it exhibit the crack propagation during the phase transformation of zirconia. The addition of CeO_2 and La_2O_3 is discussed in Sections 2.7 and 2.8, respectively in purpose to increase the rate of spontaneous transformation by adding more than one additive or stabilizer with bigger grain size and dissimilar between thermal expansion between the phases. The fabrication methodology and sintering of the ZTA ceramic is discussed in Sections 2.9 and 2.10 respectively for better comprehend about case study. In Section 2.11, the characterization method which used to investigate the properties of the samples are also explained which cover SEM, XRD, and Vickers hardness testing and fracture toughness analysis.

2.2 Research Gap

In order to achieve the improvement for the mechanical properties in terms of fracture toughness and Vickers hardness, some informations from the previous works referred as a benchmark for this current study. Table 2.1 is indicated the achievement that have been made by researchers, respectively. A specific observation by Rejab et al. (2013b) stated that the addition of CeO_2 into ZTA showed a positive impact on fracture toughness (8.38 MPa.√m) with moderate Vickers hardness (1688 HV). Although these values are still below the requirements of the up-to-date engineering applications. It has one of the most important findings whereby CeO_2 addition assists the abnormal growth of close packed spherical shape of $Ce_2Zr_3O_{10}$ grains within the ZrO_2 grains. Therefore, the fracture toughness was significantly increased (30% compare to ZTA) through the formation of $Ce_2Zr_3O_{10}$ grains that successfully inhibited the growth of Al_2O_3 grains. However, the further creation of elongated $Ce_2Zr_3O_{10}$ grains for >5.0 wt.% CeO_2 additions causes their hardness drop that leads to increase in percentage porosity.

Based on the ZTA ceramics, fracture toughness and hardness properties are generally mutually exclusive due to the inverse relationship between its brittleness and plasticity. Therefore, continues efforts have been made to enhance, and at the same time to strike a balance between their high toughness and high hardness through various methods such as: addition of oxides, nitrides and carbides, and also in-situ formation of secondary phases (Asmi et al., 2012; Chen et al., 2004; Galusek & Majling, 1995; Guo et al., 2002; Kern, 2014; Mahajan et al., 2014; Sktani et al., 2014; Wu et al., 2001; Wu et al., 2001a, 2001b).

Addition of oxides among others was mostly applied and shows various impacts to the microstructural design of ZTA. However, these oxides addition approach could not successfully balance the lop-sidedness of the two properties. Therefore, a right combination of these oxides could be a useful approach. These two phenomena are due to their specific ability to form a difference microstructural morphology and preference reaction i.e. either with Al_2O_3 or ZrO_2 grains.

Therefore, the potential benefits of co-additives for designing a new ZTA microstructure via formation of various grain shapes embedded in the original Al_2O_3 and ZrO_2 grains should be further investigated. Both the pinning and grain growth inhibitor created by various shape grains could simultaneously enhance toughness and hardness of ZTA.

Table 2.1: The fracture toughness and Vickers hardness that have been achieved by each of the ZTA ceramic

Authors	**ZTA system**	**Sintering Method**	**Indentation Fracture Resistance, K_{IFR}** (MPa.m$^{1/2}$)	**Hardness (HV)**
Mangalaraja et al.(2003)	ZTA with CeO_2	Electrical pressureless furnace	8.309	1480
Manshor et al.(2016)	ZTA with Cr_2O_3	Electrical pressureless furnace	7.15	1681
Akin et al. (2011)	ZTA with CeO_2	Spark plasma sintering	6.2	-
Manshor et al. (2015)	ZTA with TiO_2	Electrical pressureless furnace	6.56	1615.8
Rejab et al.(2013b)	ZTA with combination of CeO_2 and MgO	Electrical pressureless furnace	8.38	1688
Azhar et al. (2011)	ZTA with MgO	Electrical pressureless furnace	3.62	1740

2.3 Alumina

Alumina is the common name given to aluminium oxide (Al_2O_3). Alumina is responsible for metallic aluminium's resistance to weathering. Alumina is produced from bauxite, an ore that is mined from soil in various tropical regions. The Bayer process, discovered in 1887, is the primary process by which alumina is extracted from bauxite. It is the process of refining alumina from bauxite by selective extraction of pure aluminium oxide dissolved in sodium hydroxide (caustic soda).

To produce pure aluminium, alumina is smelted using Hall-Heroult electrolytic process. This process is referred to as primary production. The Bayer process was invented in 1887 by Carl Josef Bayer. The Austrian chemist want to seek a method for supplying alumina to the textile industry. The Bayer process gained importance in the aluminium production industry when combined with the Hall-Heroult electrolytic process. With the two processes combined, bauxite ore can be processed into alumina, which then converted into aluminium. Today, the Bayer process is virtually unchanged and is used to produce nearly all of the world's alumina supply, as an intermediate step in aluminium production (Zhong et al., 2009).

Alumina is widely applied in various production ceramic industry due to its excellent properties. Its melting point is very high which about 2054 °C and technically, it has been used to manufacture appliances with high temperature resistant. Alumina products include abrasives, insulators, structural members, refractory bricks, electronic substrates and tools. Alumina is stable, hard, lightweight and wear resistant, making it have quality for such applications as air ring, air bearings, electrical insulators, valves, thread guides and ceramic reinforcing component in metal matrix composites. Instead of its high melting point, alumina also popular of its chemically stable and inertness properties. For that reason, alumina is suitable for biomedical implant applications. In addition, superior hardness and excellent abrasion resistant of alumina causing it to be widely used as an abrasive material and bearing that serves as a more economic substitute for industrial diamond (Lazouzi et al., 2018).

2.4 Zirconia

Zirconia is a white crystalline oxide of zirconium. It is a polymorphic material that occurs in three different forms depending on temperature, tetragonal (t) above 1170 °C, and cubic (c) beyond 2370 °C. The phase transitions are reversible and in free crystals are associated with a volume expansion of about 0.5% in the case of the cubic to tetragonal (c→t) transition and about 4% for the tetragonal to monoclinic (t→m) transition.

Transformation from cubic to tetragonal to monoclinic structure will induce crack upon cooling from high temperatures due to the volume expansion generated. A relatively large volume change accompanies this transformation, resulting in the formation of cracks that make the ceramic ware useless. However, this problem is overcome by stabilizing the zirconia by adding several different alkaline rare earth oxides as dopants such as magnesia (MgO), yttria (Y_2O_3), calcium oxide (CaO) and cerium(III) oxide (Ce_2O_3) (Callister, 2011).

Nazarpour et al. (2010) stated that if sufficient quantities of metastable tetragonal phase is present and then the stress that is applied on it is intensify by stress concentrator at the crack tip, will cause the tetragonal phase to convert to monoclinic, with correlated of volume expansion. This transformation enhances the toughness by the transformation toughening mechanism. Therefore, transformation toughening play a vital role when to volume changes and toughness of ceramics when tetragonal phase transform into monoclinic (Nazarpour et al., 2010). Zirconia is very useful in this stabilised state. This phase transformation can then put the crack into compression and shut it down. Hence, the crack propagate will discontinue and enhancing fracture toughness. This effect is called transformation toughening. This effect significantly increase the reliability and durability of zirconia products.

2.5 Yttria-Stabilised Zirconia (YSZ)

Pure (undoped) ZrO_2 ceramic exhibit microcrack propagation in it system due to volume changes when the transformation of phase as mention in Section 2.4. So, yttrium oxide

(Y_2O_3) is choose to be doped to pure ZrO_2 to overcome this problem. So, it named as yttria-stabilized zirconia (YSZ). YSZ is a ceramic which the crystal structure of zirconium dioxide is made to be stable at room temperature by an addition of Y_2O_3.

Y_2O_3 are usually added in the ZrO_2 powder in order to stabilize the tetragonal and cubic phase at high temperature.

$$\text{Monoclinic} \xrightarrow{1170\ ^\circ\text{C}} \text{Tetragonal} \xrightarrow{2370\ ^\circ\text{C}} \text{Cubic} \xrightarrow{2680\ ^\circ\text{C}} \text{Liquid}$$

Figure 2.1: Phase transformation of pure zirconia (Szutkowska et al., 2006)

Transformation from cubic to tetragonal to monoclinic structure will induce crack due to the volume expansion. Hence, the strength and toughness of pure zirconia will be affected with the changes in temperature. The influence of toughening on the abrasive wear behaviour depended on the nature of the toughening mechanism activated by the zirconia addition. So, in order to achieve maximum toughness, stabilizers like yttria is chosen to being doped into the ZrO_2 matrix to maintain the metastable tetragonal phase at ambient conditions rather than the stable monoclinic phase. Transformation of metastable phase ZrO_2 to stable monoclinic phase will induces. As stated by Azhar et al. (2016), YSZ is known to have a fracture toughness that is as 20 $MPa.m^{1/2}$.

2.6 Zirconia Toughened Alumina

The main disadvantage of alumina is its low indentation fracture resistance and it can be overcome by using it in combination with yttria-stabilized zirconia (YSZ), which has a good indentation fracture resistance, to produce zirconia-toughened alumina (ZTA). ZTA belongs to a group of ceramics that have ability to self-sealing mechanism working within it. Their microstructures was properly altered to produce an effect, as mentioned before, known as transformation toughening. In order to improve the toughness, Al_2O_3 based materials are often used as a benchmark due to its abundance source, relatively cheap and superior mechanical properties.

The introduction of the yttria stabilized zirconia (YSZ) toughening agent will increase the toughness of ZTA. As stated by Azhar et al. (2009), 20 wt.% of YSZ is the optimum amount to obtain optimum wear performance. Excess addition of YSZ will cause the hardness decrease and eventually reduce the performance of the ceramic (Azhar et al., 2009). Thus, ZTA is an oxide ceramic with the most extensive applications. The major toughening mechanism that occur in ZTA are stress-induced phase transformation toughening and microcracks toughening mechanism. Zirconia toughened alumina materials have been applied for many years for wear parts and cutting tools due to their high strength, hardness, toughness and abrasion resistance (Azhar et al., 2010).

Yttria stabilized zirconia is added to the alumina to improve its low indentation fracture resistance which give results in improvement of flexural strength and facture toughness. When the stress is exerted to the ceramic, these zirconia particles convert their crystal structure from a tetragonal to monoclinic pattern. The transformation will gives results in a 3-5 vol.% expansion, which compresses the surrounding alumina, making it more resistant to cracks. The toughening process is the result of the transition of tetragonal metastable grains into a monoclinic crystal structure at the crack tip. The stress field around the crack is enough to trigger the toughening mechanism. So, whenever a crack is start to propagate in ZTA, the zirconia crystals expand and it compress the alumina matrix and squeezing the crack to close .

The effectiveness of this toughening mechanism greatly depends on the properties and the content of the dopant cations. The enhancement of the indentation fracture resistance of ZTA has been associated to transformation triggered by stress as well as strengthening of the microcracks. Their great mechanical properties, such as excellent compressive stress of 390 MPa and breaking toughness from 4 to 13 MPa.m$^{1/2}$, make ZTA ceramics are ideal for wear parts and cutting tools applications (Manshor et al., 2016).

2.7 Cerium Oxide (CeO_2)

Cerium (IV) oxide also known as or cerium dioxide is an oxide of rare earth metal cerium which belongs to the lanthanide group. Cerium (Ce) can naturally found in minerals like cerite, monazite, or basnaesite. In combination with oxygen, it is easily converted into CeO_2. Apart from CeO_2, cerium also forms the oxides Ce_2O_3 and Ce_3O_4. Cerium oxide is normally formed by calcination of of cerium oxalate or cerium hydroxide. It is generally present as micro- or nanoscale bright yellowish powder.

Previous study by Mangalaraja et al. (2003) designate that the mechanical properties (MoE, MoR, hardness and indentation fracture resistance) of yttria tetragonal zirconia polycrystals is reduced when CeO_2 is added into matrix at the range of 0 to 5 wt.%. Figure 2.2 shows the effect of CeO_2 addition on the hardness and the strength of the ZTA-CeO_2 ceramics. This material has a very stable tetragonal phase under chemical and thermal treatments. The reduction of its mechanical properties is cause by higher apparent porosity due to addition of CeO_2. The decreased mechanical properties are found to be due to the higher apparent porosity, which resulted possibly due to addtion of CeO_2. The higher degree of apparent porosity resulted due to the solid state mixing of powders.

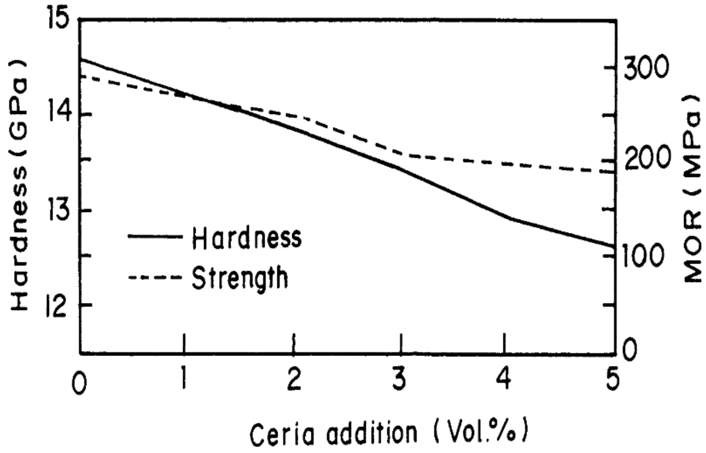


Figure 2.2: Effect of CeO_2 on the hardness and strength of ZTA

(Mangalaraja et al., 2003)

Nevertheless, previous work done by Rejab et al. (2013) stated that at 5 wt.% of CeO_2, the mechanical properties give an optimum results in terms of Vickers hardness and fracture toughness with maximum values : 1688 HV and 8.38 $MPa.m^{1/2}$. ZTA fabricated with CeO_2 additives showed an increase of 30% in fracture toughness compared to ZTA without additives. It seem there was a clash with work done by Mangalaraja et al. (2013). Literally, CeO_2 addition is very useful for improvement of fracture toughness and hardness of ZTA ceramics. The improved mechanical properties were found maybe due to the lower apparent porosity, which possibly resulted due to the addition of CeO_2.

Figure 2.3 showed the results of fracture toughness and Vickers hardness. The maximum value of toughness is at 5 wt.% of CeO_2. With further addition of up to 15 wt.% of CeO_2 addition, the indentation fracture resistance decreased to 7.9 $MPa.m^{1/2}$.

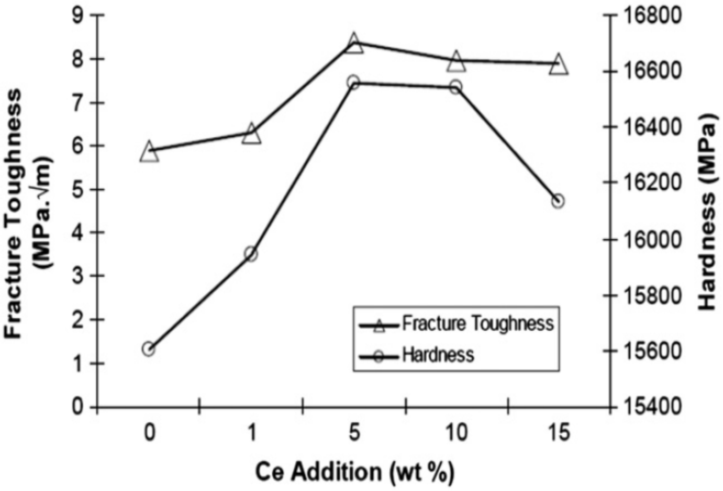


Figure 2.3: Effect of CeO_2 addition on indentation fracture resistance and Vickers hardness of ZTA (Rejab et al., 2013b)

The effect of CeO_2 addition on bulk density and apparent porosity is shown in Figure 2.4. The result of bulk density follows the pattern of theoretical density up until 5 wt.%. Further than that, the densities decrease are due to the existence of secondary phase of $Ce_2Zr_3O_{10}$. The result show that the bulk density increased and the percentage of porosity decreased with the addition of CeO_2. As consequence, this will gives contribution to the fracture toughness improvement of ZTA ceramic. The lower porosity yielded high fracture toughness and high corrosion resistance.

Equation 2.1 showed the reaction between CeO_2 and ZrO_2 with CeO_2 acts as reinforcement and combine with ZrO_2 which exist in ZTA matrix (Rejab et al., 2013b). In some study from the literature, the Ce^{4+} is reduce to Ce^{3+} by reducing agent and ready to chemically react with ZrO_2 and lead to the formation of spherical grain that scattered and evenly distribute among ZTA. Equation 2.2 show the chemical reaction between these two compounds (Mishra et al., 2002).

$$2CeO_2 + 3ZrO_2 \rightarrow Ce_2Zr_3O_{10} \quad (2.1)$$

$$Ce_2O_3 + 2ZrO_2 \rightarrow Ce_2Zr_2O_7 \quad (2.2)$$

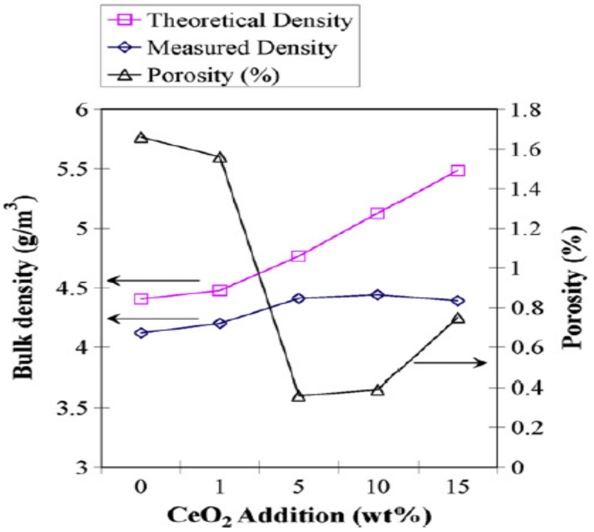


Figure 2.4: Density and porosity for ZTA-CeO_2 ceramics with different CeO_2 addition (Rejab et al., 2013b)

According to the work done by Akin et al. (2011), elongated $CeAl_{11}O_{18}$ grains will be formed when CeO_2 are added into the ZTA ceramic. Figure 2.5 shows the elongated grains of $CeAl_{11}O_{18}$. The length of the elongated grains depend on the CeO_2 composition. Higher wt.% will results in higher average length. The formation of $CeAl_{11}O_{18}$ as secondary phase could be related to the reduction of CeO_2 to the Ce_2O_3 and reaction with Al_2O_3 at higher temperatures, around 1200-1400 °C.

CeO_2 could be reduced to Ce_2O_3 and combination with Al_2O_3 during sintering resulted in formation of $CeAl_{11}O_{18}$ grains during sintering. The reason of elongated shaped of them could be related to the different ionic sizes of CeO_2. Cerium formally has the valance 4+ in CeO_2 and 3+ in Ce_2O_3. The reduction of CeO_2 to Ce_2O_3 is associated with an increase in the ionic radius 0.097 nm to 0.114 nm. The crystal structure $CeAl_{11}O_{18}$ has a unit of four oxygen layers with hexagonal closed packing. High cation sixe of CeO_2 could have caused a distortion between layers and expanded lattice. Similar report in the studies gives result that CeO_2 stabilized zirconia or yttria and CeO_2 co-stabilized zirconia ceramics. Equation 2.3 (Rejab et al., 2013a) shows the occurrence of reaction stoichiometrically.

$$Ce_2O_3 + 11Al_2O_3 \rightarrow 2CeAl_{11}O_{18} \qquad (2.3)$$

Akin et al. (2011) also stated that the addition of CeO_2 in ZTA ceramic will affect its mechanical properties. The hardness of ZTA-CeO_2 ceramic obviously decline with the addition of 3 wt.% CeO_2 and further addition resulted in lower hardness values. The decreased in hardness is due to the formation of elongated $CeAl_{11}O_{18}$ grains due to reduction of CeO_2 to Ce_2O_3 and segregation of Al_2O_3. The indentation fracture resistance of ZTA-CeO_2 lower than that un-doped ceramics about 3 and 5 wt.% CeO_2. This increment could be assumed to be the sum of the intrinsic toughness of the alumina matrix and the toughening mechanisms introduced by the zirconia particles such as transformation toughening, microcracking and internal stresses.

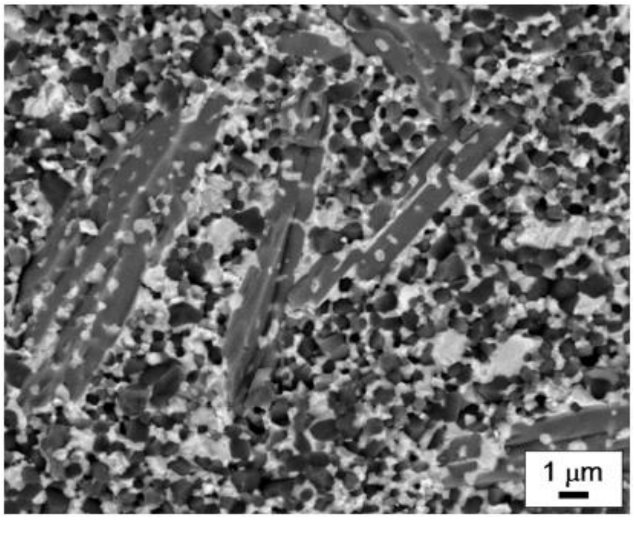


Figure 2.5: SEM image of fracture surface of ZTA-5wt.% CeO_2 sintered at 1400 °C for 300s (Akin et al., 2011)

2.8 Lanthanum Oxide (La_2O_3)

Lanthanum oxide is La_2O_3, an organic compound containing the rare earth element lanthanum and oxygen. La_2O_3 is used to develop ferroelectric materials, as a component of optical materials, and is a raw material for certain catalysts. The morphology of lanthanum oxide nanoparticles is spherical and they appear as a white powder they are greatly hygroscopic.

In the previous study by Guo et al. (2002), La_2O_3 is used as a sintering additive in the ZTA is order to improve the fracture toughness and hardness of the ceramic. The creation of elongated rod-like secondary phase that confirmed by XRD analysis as $La_2O_3.11Al_2O_3$ or $LaAl_{11}O_{18}$ is proved can improve these mechanical properties. Guo et al. (2002) stated that Al_2O_3 is compatible with many aluminate compounds such as $LaAl_{11}O_{18}$, which has an anisotropic growth habit and is suitable for toughening reinforcement. La_2O_3 is added to the ZTA and reacts with Al_2O_3 to form in situ rod-like $LaAl_{11}O_{18}$ grains that act as toughening agent to improve the mechanical properties due to their creation during sintering. However, the report stated that the increasing content of aluminate compound ($LaAl_{11}O_{18}$) has decrease the properties of the ZTA ceramics. Therefore, it is necessary to compromise the rod-like $LaAl_{11}O_{18}$ content for gaining optimal mechanical properties. Equation 2.4 shows the reaction between Al_2O_3 and La_2O_3.

$$La_2O_3 + 11Al_2O_3 \rightarrow 2LaAl_{11}O_{18} \qquad (2.4)$$

Sintering temperature has been used as parameter to investigate it influence to the fracture toughness of the ZTA-La_2O_3. Figure 2.7 shows the fracture toughness with the function of sintering temperature and rod-like $LaAl_{11}O_{18}$ content in ZTA system (Guo et al., 2002).

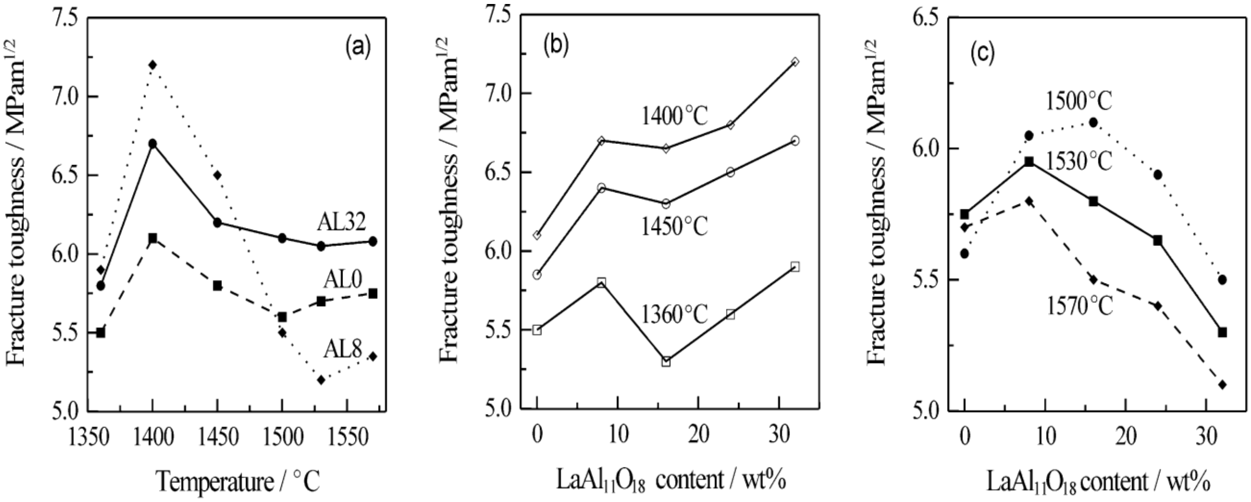
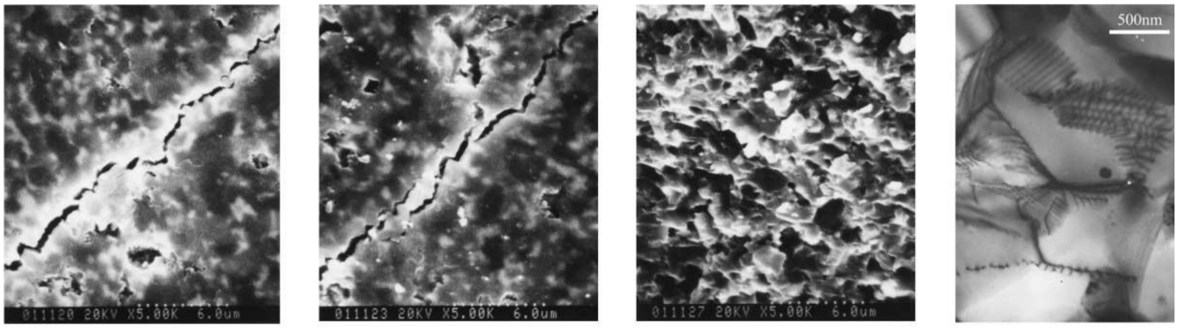


Figure 2.6: Fracture toughness vs sintering temperature and $LaAl_{11}O_{18}$ content (Guo et al., 2002)

From the analysis, when the materials were sintered at different temperatures, high content of rod-like particle led to decrease in strength but the fracture toughness increased at low sintering temperature and decrease at high sintering temperature. In situ formation of rod-like $LaAl_{11}O_{18}$ did not affect sinterability of ZTA ceramics. The bending strength over 500 MPa and the fracture toughness is 7 $MPa.m^{1/2}$ can be obtained at such low sintering temperatures. It was found from the observation of the microstructure that crack bridging and crack deflection were the main strengthening and toughening mechanism that contributing to the improvement of mechanical properties. Fracture toughness increased with sintering temperature is below 1450 ^{o}C and $LaAl_{11}O_{18}$ content was high revealing the toughening of rod-like grains increased as well.

The main contributions to strengthening and toughening of the materials come from crack bridging of rod-like grains. Figure 2.8 shows the micrographs of ZTA ceramics of indentation crack, crack deflection and crack bridging (Guo et al., 2002).



(a) AL16 (b) AL32 (c) AL16 (d) AL16

Figure 2.7: Micrographs of ZTA ceramics, SEM photographs of crack propagation after indentation (a and b), fracture Section (c) and TEM photograph (d) (Guo et al., 2002)

2.9 Fabrication of ZTA

Azhar et al. (2009) stated that ZTA ceramic with 20 wt.% YSZ are characterized to have the optimum mechanical properties from among the tested compositions. The fabrication methods were stated by Rejab et al.(2013a), Azhar et al. (2010) and Manshor et al. (2016) and these method relatively same according to the respective research.

The starting raw materials used are highly pure. Monolithic Al_2O_3 and YSZ were mixed using a ball mill for 12 hours to make sure the homogenous mixture is obtained.

The ZTA ceramic samples were fabricated by pressing the mixture of raw materials at 10 MPa into bar samples. The samples then sintered at high temperature of 1600 ^{o}C in an electrical furnace with constant heating and cooling rate of 5 ^{o}C/min. Finally, the samples were ready to be tested and characterised.

2.10 Sintering

Sintering is the process of compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction. Sintering usually done to ceramics that involve consolidate of ceramic powder particles by heating the green compact part to a high temperature below the melting point which means the corresponding particles will diffuse to the neighbouring powder particles. The particles of the powder diffuse across the boundaries, fusing the particles together and creating the solid pieces. During the diffusion process, the pores are closed up, resulting densification of the part and enhancement of its mechanical properties. The diffusion is caused by a different gradient of chemical potential-atoms that move from higher chemical potential region to lower chemical potential.

In this study, the situation of sintering is in solid state. The driving force of sintering process is the reduction of surface energy of the particles caused by decreasing their vapour solid interfaces. There are six different diffusion mechanisms during the sintering process showed as follows:

- Surface diffusion – diffusion of atoms along the surface of a particle
- Vapour transport – evaporation of atoms which condense on a different surface
- Lattice diffusion from grain boundary – atom from grain boundary diffuses through lattice

- Grain boundary diffusion – atoms diffuse along grain boundary
- Plastic deformation – dislocation motion causes flow of matter

Temperature and pressure are very highly affect the atomic diffusion. When the high temperature and pressure is applied simultaneously, the atomic diffusion will react quickly. There some important parameters in firing ceramics for processing and materials such as powder preparation, distribution of dopants or seconds phases, powder consolidation, sintering temperature, applied pressure and gaseous atmosphere.

The mechanism of sintering is illustrated in Figure 2.8. After pressing, many of the powder particles touch one another. During the initial sintering stage, necks form along the contact regions between side by side particles as shown in Figure 2.8(a). A grain boundary forms within each neck and every interstitials space between the particles becomes a pore as shown in Figure 2.8(b). As sintering advances, the pores become smaller and more spherical as shown in Figure 2.8(c). The driving force for sintering is the reduction in total particle surface area. Surface energies are larger in magnitude than grain boundary energies. Sintering is carried out below the melting temperature, so that no liquid phase not present. The mass transport that is necessary to effect the changes shown in Figure 2.8 is complete successfully by atomic diffusion from the bulk particles to the neck regions.

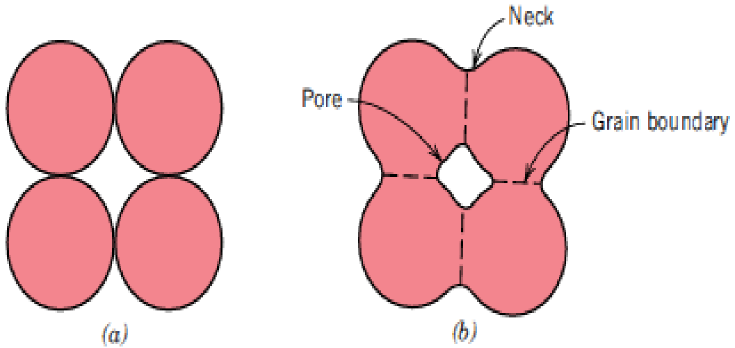


Figure 2.8(a) For a powder compact, microstructural changes that occur during firing. In (b) powder particles after pressing and in the Figure 2.8(c) the particle start to join together by necking and pore formation as sintering begins. As sintering proceeds, the pores change size.

2.11 Characterizations

Once the samples are completely sintered, characterizations process need to carry out on the ZTA-CeO_2-La_2O_3 ceramics to determine its mechanical and chemical properties. Once these properties of ceramics are characterized and understood, this information can bring the understanding of its nature to the higher level that is needed to resolve the vital issues such as failure and fabrication-related problems, as well as to make critical decisions. The characterizations process involved in this study are XRD diffractometry as describe in Section 2.11.1. In Section 2.11.2 microstructure properties is briefly describe based on the literature from previous study.

2.11.1 X-ray Diffraction (XRD)

Phase identification of ZTA-CeO_2 ceramic system is done using the powder X-ray diffractometry (XRD) analysis Samples were analysed in powder and sintered body forms.. Based on Bragg's law, all crystalline phase emitted X-ray diffraction that obey Equation 2.5:

$$n\lambda = 2d \sin \theta \tag{2.5}$$

where, n is an integer, λ is the wavelength of X-rays in Angstrom units (Å), wavelength for copper is 1.5406 Å, d is the distance between planes in Angstrom units(Å) and θ is the angle between direction or beam diffraction by crystal planes.

These X-ray are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed towards the samples. These diffracted X-rays are then detected, processed and counted. By scanning the samples through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing.

2.11.2 Microstructure Observations

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition.

According to the work done by Smuk et al. (2003), thermal etching is executed in a vacuum furnace to make the grains grow and microstructure images were obtained using