THE EFFECT OF MULTI WALLED CARBON NANOTUBES (MWCNTS) ADDITION ON THE PHYSICAL PROPERTIES, HARDNESS AND TOUGHNESS OF ZTA-MgO CUTTING TOOL

BY

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ABSTRACT

The purpose of this study is to develop ZTA-MgO-MWCNT cutting insert with enhanced properties and excellent tool performance that is suitable for high speed machining. The effects of MWCNT addition on the physical properties, hardness and fracture toughness of ZTA-MgO composites were investigated. The samples was fabricated using 80:20 composition (80 wt.% of Al_2O_3: 20 wt.% of YSZ) with fixed amount of MgO at 1.1 wt.% and MWCNT ranging from (0.1 – 0.5 wt.%) as secondary additives. The CNT was pretreated in ethanol for 1 hour using an ultrasonic homogenizer before mixing and ball milled with Al_2O_3, YSZ and MgO compositions for 24 hours. The mixture is then pressed at 100 MPa into round-shaped cutting inserts mold after being dried at 100°C for 24 hour. The pressed samples were sintered at 1600 ºC for 4 hour soaking time. There are three parts in this study whereby the first part observed phase analysis by XRD and microstructure of the sintered samples using SEM. The XRD analyses indicate the presence of major phases were α-Al_2O_3, ZrO_2, $Zr_{0.963}Y_{0.037}O_{1.982}$ and $MgAl_2O_4$. Minor peak at (002) increases with higher MWCNT wt.% which suggest the presence of MWCNT in the composites. Samples with higher content of MWCNT beyond 0.3 wt.% possessed smaller grain size and refined microstructure compared to sample with low content of MWCNT. The second part analysed the effect of MWNT addition on density, porosity and shrinkage of ZTA-MgO. Density (4.210 g/cm^3) and percentage of shrinkage (8.05%) obtained the highest value by 0.2 wt.% MWCNT compared with samples without CNT additives which is only 4.020 g/cm^3 and 7.05% respectively. High density value would mean the shrinkage percentage is also high, which corresponds to the densification of the composites. Poor dispersion of MWCNT within the matrix is highly accounted for agglomeration around Al_2O_3 grain boundaries and decreases in densification. The third part focused on hardness and fracture toughness after adding MWCNT on the ZTA-MgO composites. Results shows that ZTA-MgO samples with 0.2 wt.% MWCNT produced the highest hardness (19.93 GPa). The increment of hardness was contributed by the inhibition grain growth in Al_2O_3 due to pinning effect of MWCNT at grain boundaries. It is observed that fracture toughness increases from 3.8 MPa•√m to 8.08 MPa•√m with addition of 0.2 wt.% MWCNT. The improvement of fracture toughness is possibly due to the transformation toughening mechanism of t - ZrO_2 to m - ZrO_2. Results of hardness and fracture toughness exhibit that ZTA-MgO with additions of 0.2 wt.% MWCNT is the best composition for ceramic cutting tools application.

خلاصة البحث

تهدف هذه الدراسة إلى تطوير أداة قطع ZTA-MgO-MWCNT وإعطائها خصائص محسنة وأداء ممتاز ليتناسب مع التشغيل عالي السرعة. تم استكشاف الآثار المترتبة على إضافة MWCNT إلى البنية المجهرية، وكذلك الخواص الفيزيائية والصلابة ومتانة الكسر لمركب ZTA-MgO. تم تصنيع العينات باستخدام مركب بنسبة 80:20 (أي 80% من Al_2O_3 ; 20% من YSZ) مع كمية ثابتة من MgO بنسبة 1.1 و نسبة MWCNT تتراوح بين 0.1 و 0.5% كإضافات ثانوية. تمت ف البداية معالجة الأنابيب النانوية الكربونية CNT في الإيثانول لمدة ساعة باستخدام خالط فوق صوتي قبل خلطها وطحنها بالكرات مع مركبات Al_2O_3 و YSZو MgO لمدة 24 ساعة. بعد ذلك تم ضغط الخليط بمعدل 100 ميجا باسكال في قالب قطع دائري الشكل، وذلك بعد تجفيفه في 100 درجة مئوية لمدة 24 ساعة. تم تلبيد العينات المضغوطة في درجة مئوية تبلغ 1600 لمدة 4 ساعات. تنقسم هذه الجراسة إلى ثلاثة مراحل; شهدت المرحلة الأولى تحليلًا للمراحل بواسطة XRD والبنية المجهرية للعينات الملبدة باستخدام SEM. أشار تحليل XRDإلى وجود مراحل أساسية وهي α-Al_2O_3, ZrO_2, $Zr_{0.963}Y_{0.037}O_{1.982}$ و$MgAl_2O$. ظهرت ذروة بسيطة في نقطة (002) والتي زادت بزيادة نسبة MWCNT وذلك يشير إلى وجود MWCNT في المركبات. أظهرت العينات التي تحتوي على MWCNT بنسبة أعلى من 0.3% حجمًا أصغر للحبة وبنية مجهرية أفضل مقارنة بالعينة التي تحتوي على نسبة MWCNT منخفضة. أما المرحلة الثانية فقدت شهدت تحليلًا لتأثير إضافة MWNT على الكثافة والمسامية ونسبة الانكماش الخاصة بمركب ZTA-MgO. حصل معدل الكثافة ($4.210\ g/cm^3$) ونسبة الإنكماش (8.05%) على أعلى القيم مع نسبة 2% إضافية من MWCNT مقارنة بالعينات التي لا تحتوي على أي إضافات من CNT، والتي بلغت $4.020\ g/cm^3$ و7.05% تباعًا. تشير قيمة الكثافة العالية إلى أن نسبة الانكماش أيضًا عالية وهذا يعود إلى تكثيف المركبات. تسبب التشتت الضعيف الخاص ب MWCNT في المصفوفة درجة تكتل عالية حول حدود حبوب Al_2O_3 وكذلك انخفاضًا في التكثيف. وأخيرًا، فإن الجزء الثالث ركز على الصلادة ومتانة الكسر بعد إضافة MWCNT على مركب ZTA-MgO. **أشارت النتائج إلى أن عينات ZTA-MgO التي تحتوي على نسبة إضافية من** 0.2% من MWCNT أنتجت أعلى نسبة للصلادة والتي تبلغ 19.93 (GPa. ترجع الزيادة في الصلادة إلى كبح نمو الحبوب في Al_2O_3 بسبب تأثير التثبيت من قبل MWCNT على حدود الحبوب. تم ملاحظة أن متانة الكسر زادت من 3.8 MPa•√m إلى 8.08 MPa•√m عند إضافة 0.2% من MWCNT. قد يكون التحسين الملحوظ في متانة الكسر بسبب تحويل آلية التصلب الخاصة ب t-ZrO_2 إلى m-ZrO_2. تشير نتائج الصلادة ومتانة الكسر إلى أن ZTA-MgO -التي بها نسبة 0.2% إضافية من MWCNT - هي أفضل تكوين لتطبيق أدوات قطع السيراميك.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Master of Science (Materials Engineering)

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DECLARATION

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LIST OF ABBREVIATIONS

Al	Aluminum
Al_2O_3	Alumina
CaO	Calcium Oxide
CeO_2	Ceria
CNT	Carbon Nanotubes
Cr_2O_3	Chromium Oxide
g/cm^3	Gram/Cubic Centimetre
GPa	Giga Pascal
HIP	Hot Isostatic Pressing
HV	Vickers Hardness
ICDD	International Centre Diffraction Data
kgf	Kilogram force
mol%	Mole Percentage
MgO	Magnesium Oxide
$MgAl_2O_4$	Magnesium Aluminate/Spinel
$(MgOH)_2$	Magnesium Hydroxide/Brucite
MPa	Mega Pascal
MWCNT	Multi-Walled Carbon Nanotubes
N	Nitrogen
O	Oxygen
Pd	Palladium
ppm	Parts per million
rpm	Revolutions per minute

SEM	Scanning Electron Microscope
Si	Silicon
S/m	Siemens per meter
Si_3N_4	Silicon Nitride
SPS	Spark Plasma Sintering
SWCNT	Single-Walled Nanotubes
TiO_2	Titanium Dioxide
TPa	Tera Pascal
USA	United States of America
vol %	Volume Percentage
wt.%	Weight Percentage
W/mK	Watts per meter-Kelvin
XRD	X-Ray Diffraction
YSZ	Yttria Stabilized Zirconia
ZrO_2	Zirconia
ZTA	Zirconia-Toughened Alumina
ZTA5CeO2	Zirconia-Toughened Alumina with 5 wt.% Ceria

LIST OF SYMBOLS

Θ	Angle
ρ	Density
°C	Degree Celsius
A	Area
Å	Angstrom unit
c	Cubic
c	Crack Length
Cu	Copper
d_i	Diameter Before Sintering
d_f	Diameter After Firing
D	Length of Impression Diagonal
E	Young’s Modulus
F	Force
K_{Ic}	Fracture Toughness
m	Monoclinic Phase
P	Indentation Load
s	Seconds
t	Tetragonal Phase
W_d	Dry Weight of the Samples
W_w	Saturated Weight of the Samples
W_s	Suspended Weight of the Samples

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

The application of ceramic as a cutting tool is escalating over the years owing to its excellent properties in wear resistance, thermal shock resistance and heat resistance. These properties enabled them to machine hard metals at high temperatures and show little reduction of hardness with increasing temperature. There are various kinds of ceramic materials such as silicon nitride (Si_3N_4) and sialon (a combination of Si, Al, O and N) whilst alumina (Al_2O_3) is the most common ceramics used for cutting tools application. Al_2O_3 based ceramic cutting tool has high temperature resistance (Li *et al.*, 2017), high hardness (Leonov *et al.*, 2019) and provide good abrasion resistance (Guo *et al.*, 2019). Apart from their good properties, Al_2O_3 base cutting tools have poor toughness as compared with metals and are sensitive to mechanical or thermal shock which has limited their application as cutting tool.

In order to toughen Al_2O_3 composites, several attempts have been carried out by incorporating high toughness reinforcement. For instance, yttria stabilized zirconia (YSZ) was introduced into Al_2O_3 and produced zirconia-toughened alumina (ZTA). It is reported that strength and toughness have been improved due to the stress induced tetragonal to monoclinic martensitic transformation toughening and micro crack toughening (Arab *et al.*, 2015). These qualities provide better machining performance than pure Al_2O_3 tools. Numerous studies focused on improving ZTA performance further without diminishing its existing properties through reinforcement with fibres, whiskers and the introduction of mixed oxide additives which act as stabilizer such as chromium oxide (Cr_2O_3) (Manshor *et al.*, 2016), ceria (CeO_2) (Azhar *et al.*, 2018), titania (TiO_2) (Mahmood *et al.*, 2017a) and magnesium oxide (MgO).

A research carried out by Singh *et al*. (2018), showed significant improvement in mechanical properties, like hardness, fracture toughness and flexural strength, when 0.6 wt.% MgO was reinforced in ZTA matrix. Arab *et al*. (2019), studied microstructure of ZTA-MgO and observed less porosity, smaller grain size of Al_2O_3 and denser ZTA samples due to the pinning effect of MgO. The physical properties of ZTA is expected to change contributed from formation of secondary phase, $MgAl_2O_4$ with addition of 0.5 wt.% of MgO onwards (Azhar *et al.*, 2018). A study by Azhar *et al*. (2011b), found that MgO particle sizes plays a significant role in the improvement of mechanical properties, whereby smaller particle size distributed better throughout the composites and induce better wear performance.

Even though the performance of ZTA cutting tool such as microstructure, hardness and tool wear have been improved via the introduction of MgO into the matrix, the fracture toughness of the ZTA-MgO ceramics are still not comparable to standard cutting tool in industry. Following the recent advancement of material, this weakness can be overcome by adding nanomaterial as secondary additives. According to Guo *et al*. (2020) and Saheb *et al*. (2019), the introduction of nanomaterial such as carbon nanotubes (CNTs) have significant effect on the mechanical properties, grain size, and density of the ceramic cutting tool. CNT have been an interesting subject of research due to combination of excellent mechanical, tensile strength, thermal conductivity and electrical properties. CNTs can be classified into two kinds; single-walled nanotubes (SWCNTs) and multi-walled structures nanotubes (MWCNTs). Although SWCNTs possessed better properties but MWCNTs are more preferable due to the relative simplicity in preparation, easier to disperse and functionalize into carbon nanotube structure.

Momohjimoh *et al*. (2019), found that Al_2O_3 with addition of 2 wt.% MWCNT by spark plasma sintering (SPS) method showed an increased in the hardness and fracture toughness of 12% and 32%, respectively. The significant effect on the mechanical and thermal properties of Al_2O_3 composites can be explained due to the high aspect ratios of CNT which hinder the grain growth during sintering at high temperatures as CNTs have a pinning effect on the alumina matrix which results in improved of mechanical properties. A study by Ghobadi *et al*. (2017), reported that using MWCNT as the reinforcement has increased the toughness of monolithic alumina by ~37%. The mechanical properties of the CNT–reinforced Al_2O_3 with MgO additions showed improvement on hardness, flexural strength and fracture toughness against the monolithic Al_2O_3 (Ahmad *et al.*, 2015). This finding is similar to the work done by (Galusek and Galusková, 2015) whereby they found that by incorporating MWCNT into conventionally sintered ZTA resulted in an increase of fracture toughness, with MWCNT acting as an efficient toughening agent.

These suggest that the extraordinary strength of CNTs, have upgraded the Al_2O_3 composites to a mechanically superior matrix that will be suitable for cutting tool application. Therefore, it is expected ZTA-MgO composite would possess such advantageous characteristics as improved toughness and hardness by integrating MWCNT in the matrix.

1.2 STATEMENT OF THE PROBLEM

MWCNTs exhibit exceptional mechanical properties such as very high tensile strength and Young's modulus up to 200 GPa and 1 TPa respectively that make them attractive toughening agents in alumina-based composites (Purohit *et al*., 2014). Singh *et al*. (2018), reported that 0.1% MWCNT addition in ZTA has a significant effect in fracture toughness and hardness of the samples. The toughening mechanism was mainly attributed to pull-out and crack deflection. At the same time, Couto *et al*. (2018) reported similar findings that ZTA containing 0.1 wt.% CNT sintered at 1600°C has better results compared to pure alumina; their best results were hardness of 16.6 GPa and fracture toughness of 5.5 MPa.m$^{0.5}$. MWCNT was introduced into alumina based ceramics to transfer the exceptional elasticity and strength of the CNTs to overcome their nature of brittleness and improve their mechanical properties that will be suitable for high speed machining.

However, there were challenges in processing of CNT-reinforced composites which are achieving homogenous dispersion of CNTs within the matrix, poor densification and preserving of CNTs during sintering. CNTs tend to form agglomerates due to their high surface area, geometry and van der Waals forces (Akin *et al.*, 2015). Homogenous distributions of CNTs in the matrix have significant influence for achieving the desired properties of composites (Ahmad *et al.*, 2015). Most work reported that addition of CNTs as reinforcements enhanced the fracture toughness but reduced the hardness and strength.

Therefore, numerous researches have been conducted to improve the performance of CNTs as a reinforcement agent and further enhanced the alumina-based composites mechanical properties. For example, Ahmad *et al*. (2016) reported that small amounts of 600 ppm MgO doping into Al_2O_3/MWCNT resulting in high densities near theoretical value (99.6%), improvement around 37, 22, and 20% in fracture toughness, flexural strength, and hardness respectively compare to pure Al_2O_3. They found that MgO has played a significant role in reducing the sintering temperatures and refining the grain size of the matrix which improved the densification of MWCNT/Al_2O_3 nanocomposites. MgO is also capable to tune the apparent disadvantages of MWCNT and produce homogenous microstructures in nanocomposites, which led to higher densities and enhanced mechanical properties. Similarly, Singh *et al.* (2018) observed uniformly distributed particles with small grains up to 0.6 wt.% of MgO. The researcher also showed improvement in mechanical properties, such as hardness (17.04 GPa), fracture toughness (5.09 MPa $m^{1/2}$) and flexural strength (502 MPa) with addition of small amount MgO in ZTA because of the tetragonality effect.

Although many researchers have focused on the CNTs additives on the Al_2O_3 and MgO alone, none have attempted to investigate the effect of MgO together with MWCNT on the properties of ZTA cutting insert. Therefore, this is the pioneer work in evaluating the effect of MWCNT's as secondary additives on the physical properties, hardness and toughness of in ZTA - MgO ceramics composite for cutting insert application.

1.3 RESEARCH OBJECTIVES

The main objective of this research is to evaluate the potential performance of MWCNTs as secondary additives to the ZTA-MgO ceramic cutting inserts for high speed machining application. The specific objectives have been defined for these studies are as follows:

i. To investigate the effect of addition MWCNTs (0 – 0.5 wt.%) on the phase analysis and microstructure of newly developed ZTA-MgO-MWCNTs cutting insert.

ii. To analyse the effect of addition MWCNTs (0 – 0.5 wt.%) on the physical properties of ZTA-MgO.

iii. To identify the optimum composition of ZTA-MgO-MWCNT ceramic cutting tools with improved hardness and fracture toughness.

1.4 SCOPE OF THE STUDY

This research is divided into two parts. Part 1 is to analyze the effect of MWCNTs addition on the phase analysis and microstructure of ZTA-MgO ceramic composites. Samples were prepared based on 80:20 ratio of Al_2O_3: YSZ with a constant value of 1.1 wt.% of MgO and different wt.% of CNT ranging from 0 wt.% to 0.5 wt.%. The samples were prepared by wet mixing method and pressed at 100 MPa for 120 seconds. Then, the samples were sintered at 1600 ºC for 4 hours soaking time. Phase analysis was determined by X-Ray Diffraction (XRD). Scanning electron microscope (SEM) was used to study microstructure of the samples.

Part 2 is to observe the effect of addition MWCNTs on the physical properties, hardness and fracture toughness of ZTA-MgO. Vickers hardness was identified by Vickers indentation test with 30 kgf load applied for 10 seconds. The fracture toughness was calculated based on the crack performed on the indented surface samples. The optimum MWCNTs content where, hardness and fracture toughness of the ZTA-MgO-MWCNTs composites had significantly improved was identified.

1.5 LIMITATIONS OF THE STUDY

The findings of this study have to be seen in light of some limitations. In current study, the purity of MWCNT and MgO used is 98% and 95% respectively. The remaining percentage is impurities and was not taken into consideration during calculation of mixture ratio. Starting material with high purity (99.9%) is recommended to use since the remaining impurities presence in the composites mixtures may affect the properties of final product.

Another limitation was, pre-treatment of CNTs. Dispersion method using ethanol as solution was used in this study and results in agglomeration of the ceramic composites. In order to fully utilize the beneficial transport properties of this material and avoid agglomeration it is necessary to establish an appropriate pre-treatment approach for MWCNTs.

1.6 THESIS ORGANIZATION

This research comprises of five chapters which aimed to see the weight percentage of CNT addition that gives the best properties to the ceramic cutting tool. Here is an overview of the content of each presented chapter:

- Chapter One: This chapter introduces the problems with alumina ceramic cutting tool in high speed machining, describes the needs of excellent properties of cutting tool and gives an overview about the improvement of hardness and fracture toughness by MWCNTs as secondary additives. This chapter also discusses the scope of the study and its objectives.
- Chapter Two: This chapter covers the literature review which is pertinent to the study. The chapter highlighted the development of ceramic cutting tool, followed by the discussion on previous method done to improve the properties

of ceramics and the advantages of MWCNT as additives. It ends with summary for Chapter 2.

- Chapter Three: This chapter explains the details of the selected methodology used in order to achieve the objectives of this research.
- Chapter Four: This chapter present the findings of data gathered and provides analysis of the findings based on previous research.
- Chapter Five: This chapter concludes and finalizes this research based on the results and the analyzed data obtained from Chapter 1 to Chapter 4. These chapters also conclude the effect of MWCNT in ZTA-MgO composites as cutting tools and provide recommendations to improve future research.