



**Fabrication and Characterization of Tungsten-brass Composites
using Powder Metallurgy process**

by

054514

rb

FTA418.9

C6G723

2016

Baba Gowon

1340410867

A thesis submitted in fulfilment of the requirements for the degree of Doctor of
Philosophy in Materials Engineering

**School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS**

2016

ACKNOWLEDGEMENT

Glory be to God almighty for enabling me to complete my PhD studies. A million thanks as well to those who contributed directly and indirectly towards the completion of this thesis. First and foremost, I like to express my profound gratitude to my supervisor, Dr. Muhammed S. Kahtan and co-supervisors, Prof. Dr. Shamsul Baharin Jamaluddin and Prof. Dr. Zuhailawati Hussain for immeasurable guidance, support and encouragements throughout this programme. Prof. Dr. Azmi Ramat is equally acknowledged for his fatherly encouragement and support throughout this programme. I also like to express my gratitude to the Dean, Dr. Khairil Rafezi Ahmad and the entire staff of the School of Materials Engineering for their support and assistance. Dr. Rozyanty, Dr. Fitri and Dr. Dewi are highly appreciated for their guidance and corrections.

My special thanks go to my family, especially my parents, my brothers and sisters, (particularly Alh. Baba Ejiga) for my academic training, my wife, Mrs Eke Justina Baba for her continuous support, patience and taking care of our children alone while I was away. Special thanks also to my children; Itodo, who cried bitterly the first day I was leaving for Malaysia even though he was just a year old then, Ameh and Ojima-ojo.

At this juncture, I'm extremely grateful to the Nigerian government and my school, the Federal Polytechnic Idah for giving me the *tetfund* scholarship for this programme. The understanding and co-operation of the Polytechnic Registrar, Alh. Karim Abu is highly appreciated. My sincere gratitude goes to my friends and colleagues, Engr. Aji Dan, Engr. Y. A. Lawal and Engr. Friday Daniel, who solidly stood by me in prayers, encouragement and taking care of my family during this period.

I'm also thankful to all the technicians in the School of Materials Engineering, UniMap, and those of the Mineral Resources and Materials Engineering, Universiti Sains Malaysia (USM), especially Mr. Sharul Ami Zainal Abidin for his love, patience and guidance throughout the laboratory works.

My humble appreciation and thanks go to all my friends, Ass. Prof. Mustafa Al Bakri, Alida, Polycarp Evarastics, Oluseyi, Samuel Ogbara, Mr. Lee, Success Ugbane Sani, Engr. D. O. Attah, Engr. A. O. Opaluwa, Elder J. I. Itanyi, Wan Zakaria, Uncle Tan, Uncle Mow Ting, Pastor Leonard Lim, Uncle Cheah, Aunty Janeth and members of the Perlis Grace Center (PGC) for their support and prayers.

Finally, my appreciation goes to everybody that contributed in various ways to my studies. Without all these wonderful people, both named and unnamed, it would have been impossible for me to complete my studies here. To all these people, I say, God bless you.

TABLE OF CONTENTS

	PAGE
THESIS DECLARATION	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	vi
LIST OF FIGURES	xii
LIST OF TABLES	xvi
LIST OF ABBREVIATIONS	xvii
ABSTRAK	xviii
ABSTRACT	xix
CHAPTER 1: INTRODUCTION	1
1.1 Tungsten-brass Composites	3
1.2 Importance of the Study	4
1.3 Problem Statement	5
1.4 Objective of the Study	6
1.5 Scope of the Study	6
CHAPTER 2: LITERATURE REVIEW	
2.1 Introduction	8
2.2 Composites	9
2.3 Metal Matrix Composites	10
2.3.1 Uses of metal matrix composites	11
2.4 Powder Metallurgy	11
2.4.1 Powder Compaction	13
2.4.2 Die Compaction	13

2.4.3	Compressibility	14
2.4.4	Porosity	15
2.5	Sintering	16
2.5.1	Solid state sintering	20
2.5.2	Supersolidus Liquis Phase Sintering	21
2.5.3	Liquid Phase Sintering	22
2.5.4	Activated Sintering by Transition metals addition	23
2.5.5	Mechanical alloying	25
2.5.6	Liquid Infiltration Method of Sintering	28
2.6	Contact angle and dihedral angle	31
2.6.1	Contiguity and Connectivity	32
2.7	Mechanical properties	33
2.7.1	Wear	33
2.7.2	Vickers hardness test	34
2.7.3	Brazilian test (Diametral tensile strength test)	36
2.8	Physical properties	37
2.8.1	Electrical conductivity	37
2.8.2	Thermal conductivity	38
2.8.3	Corrosion	39
2.8.4	Metallography	40
2.9	Phase diagrams	41
2.9.1	Cu- Zn phase diagram	41
2.9.2	Cu-Ni Phase diagram	42
2.9.3	W-Fe phase diagram	43
2.9.4	W-Cu phase diagram	43

2.10	Materials and their properties	44
2.10.1	Tungsten	44
2.10.2	Copper	45
2.10.3	Brass	45
2.10.4	Zinc	46
2.10.5	Nickel	46
2.10.6	Iron	46
CHAPTER 3: MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES		
3.1	Introduction	48
3.2	Characterization of the Raw Materials	48
3.2.1	As received powders used in this study	48
3.3	Green compaction	51
3.4	Sintering process	52
3.5	Green Density and Sintered Density Measurement	54
3.5.1	Determination of Shrinkage and Porosity	56
3.6	Microstructural Analysis of the Sintered Compacts	57
3.7	Activated Sintering by the Addition of Transition Metals	57
3.8	Mechanical Alloying by Ball Milling	58
3.9	Sintering by Direct Infiltration and Infiltration by Shell-on-core	59
3.9.1	Sintering by Direct Infiltration Process	59
3.9.2	Infiltration by Shell-on-core	60
3.10	MECHANICAL PROPERTIES	62
3.9.1	Vickers microhardness Test	62
3.10.2	Brazilian Test (Diametral Tensile Strength Test)	63

3.11	Wear Test of W-brass	64
3.12	Corrosion Test	66
3.13	Physical Properties of W-brass	68
3.13.1	Coefficient of thermal expansion (CTE)	68
3.13.2	Electrical conductivity	68

CHAPTER 4: RESULTS AND DISCUSSION

4.1	Introduction	71
4.2	Characterization of the As Received Powders	71
4.2.1	SEM and EDX of the Raw Materials	71
4.2.2	Particle size analysis	74
4.2.3	Thermal analysis	76
4.3	Conventional Solid State Sinterings	79
4.3.1	Introduction	79
4.3.2	Morphology	81
4.4	Activated Solid State Sintering	84
4.4.1	Relative sintered density	85
4.4.2	EDX and hardness	88
4.5	Conventional and Activated LPS	90
4.5.1	Relative sintered density and porosity	91
4.5.2	Morphology	94
4.5.3	XRD and hardness properties	96
4.6	Mechanically Activated Sintering	97
4.6.1	Effect of milling time on the relative sintered density	98
4.6.2	Effects of milling time on morphology	101

4.6.3	Effects of milling time on XRD and hardness properties	104
4.7	The Effects of Sintering Temperature on Mechanically Activated Sintering	106
4.7.1	Effects of sintering temperature on relative sintered density	107
4.7.2	Effects of milling time and sintering temperature on morphology	109
4.7.3	EDX and hardness properties	112
4.8	Direct Infiltration	114
4.8.1	Effects of direct infiltration of relative sintered density and hardness	114
4.8.2	Effects of direct infiltration on morphology	117
4.9	Infiltration by shell-on-core	122
4.9.1	Effects of shell-on-core on the sintered density and hardness	123
4.9.2	EDX and morphology	125
4.10	Tensile Properties of W-brass	128
4.10.1	Morphology of the fractured surfaces	129
4.11	Wear behaviour of W-brass	131
4.12	Corrosion resistance of W-brass	139
4.12.1	Corrosion rate of W-brass	139
4.12.2	Morphology of the corroded surfaces	144
4.13	Physical properties of W-brass	150
4.13.1	Coefficient of thermal expansion (CTE)	150
4.13.2	Electrical conductivity	153

CHAPTER 5: CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH

5.1	Conclusions	157
5.2	Recommendations for future research	158

REFERENCES

160

APPENDIX

179

©This item is protected by original copyright

LIST OF FIGURES

NO.		PAGE
2.1	Two-sphere model of initial stage sintering	18
2.2	Showing how low contact angle supports wetting while high contact angle resists wetting	32
2.3	Schematic illustration of Vicker hardness test measurement	35
2.4	Cu-Zn phase diagram	41
2.5	Cu-Ni phase diagram showing complete miscibility	42
2.6	W-Fe phase diagram	43
2.7	W-Cu phase diagram	44
3.1	Flow chart showing research activities outline	50
3.2	Powder compaction steel mould	51
3.3	Mechanical press, maximum load of 10 tones	51
3.4	Carbolite horizontal alumina tube furnace	53
3.5	The time-temperature heating curve	53
3.6	Precisa Gravimetries AG	55
3.7	Ceramic mould	61
3.8	Spherical shell-on-core compact	62
3.9	Axial torsion testing machine	63
3.10	Typical fracture mode in Brazilian tests	64
3.11	Wear testing machine	65
3.12	Worn surface of the stainless steel counter body	65
3.13	Corrosion Test Assembly	67
3.14:	Dilatometer L75 Horizontal	68
3.15:	Two point probe	69

4.1	SEM and EDX analysis of tungsten, copper and brass powder	72
4.2	SEM and EDX analysis of Fe, Ni and Zn	73
4.3	Particle size distribution of tungsten powder, copper powder, and brass powder	74
4.4	Particle size distribution of MA powders of W-brass milled for 8 hours, W-brass milled for 12 hours and W-brass milled for 14 hours	75
4.5	DTA and TGA curve of pre-alloyed powder (60W-brass)	77
4.6	DTA and TGA of pre-mixed powder (60W-brass)	77
4.7	DTA and TGA of pre-alloyed brass	78
4.8	Relation between the composition, relative green density, relative sintered density and hardness of PM W-brass composites	79
4.9	SEM of the green compact	81
4.10	SEM of sintered compacts of 50 wt. % W, 60 wt. % W, 70 wt.% W and 80 wt. % W	82
4.11	EDX images of the sintered compacts of 50 wt. % W and 70 wt. % W	83
4.12	The relation between W, Fe composition and relative green density	85
4.13	The relation between W, Fe composition and relative sintered density	86
4.14	EDX spot scan of W, Cu and Fe	88
4.15	The effect of Fe on hardness of the sintered compacts with 60 wt. % W	89
4.16	Relation between composition and relative sintered density for both activated and non-activated W-brass, and Relation between composition and densification parameter (DP) for both activated and non-activated W-brass composites	92
4.17	Relation between composition and porosity in green compacts and sintered compacts	93
4.18	SEM of W-brass composites 50W-50br, 50W-49br-1Fe, 60W-40br, 60W-39br-1Fe, 70W-30br, and 70W-29br-1Fe	95

4.19	XRD pattern for (a) non-activated W-brass and (b) activated W-brass	96
4.20	Effect of Fe on microhardness	97
4.21	Relative density with milling time, and densification parameter with milling time	98
4.22	The relation between green and sintered porosity with milling time	99
4.23	SEM of the milled powders of W-Ni milled for 4 h, W-Ni-brass milled for 4h, W-Ni milled for 6h, W-Ni-brass milled for 6h, W-Ni milled for 7h and W-Ni-brass milled for 7h	102
4.24	SEM of the sintered compacts, of as-received W-Ni-brass compact (without MA), W-Ni-brass milled for 8h, W-Ni-brass milled for 12h and W-Ni-brass milled for 14h	103
4.25	XRD results of milled powder for 8, 12 and 14h, sintered compacts from powders milled from 8-14h and as-received compact	105
4.26	Variation of microhardness with milling time	106
4.27	Relative green and sintered density of the composites	108
4.28	SEM of pre-mixed powders milled for 8 hours and milled for 10 hours	109
4.29	SEM of the sintered samples (a) -(b) pre-alloyed and pre-mixed composites sintered at 800 °C, (c) -(d) 920 °C and (e) -(f) 1000 °C respectively	110
4.30	EDX of pre-alloyed and pre-mixed composite composites sintered at 1000 °C	112
4.31	Microhardness values for PA and PM composites	114
4.32	SEM image of direct infiltrated samples	118
4.33	SEM/EDX of infiltrated PA W-alpha brass	119
4.34	SEM/EDX of infiltrated PM W-alpha brass	120
4.35	XRD of brass infiltration-top and bottom, and copper infiltration-top and bottom	121
4.36	EDX of PM W-brass powder milled for 13 h	125

4.37	SEM of sintered as received PM compact, (b) PA compact milled for 13h, PM compact milled for 13h and the porosities in PM compact milled for 13h	126
4.38	SEM fractography of the samples milled for 13h, 60W-39br-1Ni PA and 60W-39br-1Ni PM	129
4.39	SEM of fractography of 80W-19br-1Ni PM, and 60W-39br-1Ni PM	130
4.40	Wear volume loss and wear rate of W-brass composites	132
4.41	SEM of the worn surfaces of W-brass composites	134
4.42	EDX analysis of the worn surface of 70W-30br	135
4.43	SEM of the wear debris	138
4.44	Corrosion rates of W-brass composites	140
4.45	Optical micrographs of the corroded W-brass composites	144
4.46	SEM of the corrosion products	145
4.47	EDX of 50W-50br after 7 days immersion	146
4.48	EDX of 50W-50br after 21 days immersion	147
4.49	EDX of 50W-50br after 35 days immersion	148
4.50	XRD of 60W-40br for 7, 21 and 35 days immersion	149
4.51	The relation between linear thermal expansion and temperature	152
4.52	The effects of composition, activators and MA on the electrical conductivity of W-brass composites	154

LIST OF TABLES

NO.		PAGE
3.1	Characteristic of the as received powders used in this study	49
4.1	properties of W-brass composites	117
4.2	The relation between the composition, density and hardness of the W-brass composites produced by shell-on-core	123
4.3	Results of dimetral tensile strength	128
4.4	Density, microhardness and roughness values of the worn specimens	139
4.5	The CTE values and the sintered densities of W-brass samples	151

©This item is protected by original copyright

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
br	Brass
BIB	Brass Infiltrated at the Top
BIT	Brass Infiltrated at the Bottom
CIB	Copper Infiltrated at the Bottom
CIT	Copper Infiltrated at the Top
CTE	Coefficient of Thermal Expansion
DTA	Differential Thermal Analyzer
DI	Direct Infiltration
Dp	Densification parameter
EDM	Electric Discharge Machining
EDX	Energy Dispersive X-ray
IACS	International Annealed Copper Standard
KEP	Kinetic Energy Penetrator
LPS	Liquid Phase Sintering
MA	Mechanical Alloying
MMLs	Mechanically Mixed Layers
MMCs	Metal Matrix Composites
PA	Pre-alloyed
PM	Pre-mixed
SEM	Scanning electron microscope
SSS	Solid State Sintering
SLPS	Super-solidus Liquid Phase Sintering
TD	Theoretical density
TGA	Thermogravimetric Analyses

Fabrikasi dan Pencirian Komposit Tungsten-loyang melalui Kaedah Metalurgi Serbuk

ABSTRAK

W-kuprum komposit telah digunakan pakai bagi penghasilan peluru, bahan-bahan elektrod untuk mesin pelepasan elektrik (EDM), sentuh elektrik, pakej mikroelektronik, pengimbang berat dalam ruang kraf dan dalam kenderaan sukan. Komposit W-loyang adalah calon bahan alternatif yang lebih murah bagi aplikasi-aplikasi di atas kerana suhu pensinteran yang lebih rendah dan kos loyang yang lebih rendah berbanding kuprum. Kajian ini dilakukan berdasarkan objektif utama iaitu menghasilkan bahan baru yang boleh menjadi bahan alternatif kepada komposit W-kuprum dengan penempatan W-loyang menghampiri ketumpatan teori. Kajian ini menunjukkan keadaan pepejal konvensional dan pensinteran fasa cecair tidak boleh digunakan untuk pepadatan komposit W-loyang kerana ketakbolehlarutan diantara W, kuprum dan Zink, pengembangan padat, penyahzinkan dan kebolehasahan yang rendah W oleh loyang cair. Permasalahan penempatan yang rendah telah diselesaikan melalui kaedah pengalioan mekanikal, penyusupan langsung dan penyusupan melalui teras kelompong, "shell-on-core". Serbuk dipadatkan ke dalam acuan yang mempunyai 10 mm garis pusat dan ketinggian 3 – 4 mm bagi menghasilkan sampel "green-compact". "Green compact" ini seterusnya disinter pada suhu 800 °C, 920, 1000 dan 1150 °C bawah persekitaran hidrogen tulen selama 1 - 2 jam. "Green compact" bagi kedua-dua pra-campuran dan pra aloi dikenakan kadar pemanasan dan penyejukan yang berbeza-beza. Pengalioan mekanikal telah dijalankan selama 4, 5, 8, 10, 12, 13 dan 15 jam untuk serbuk pra-campuran dan pra aloi di bawah persekitaran argon tulen. Sampel yang telah disinter diuji dari segi ketumpatan, kekerasan, kekuatan tegangan, ketahanan haus, ketahanan kakisan, kekonduksian elektrik dan pekali pengembangan haba. Proses penyusupan langsung, penyusupan melalui teras kelompong dan mekanikal menyebabkan ketumpatan sinter yang lebih tinggi sehingga 99% TD. Kekerasan komposit telah meningkat apabila meningkatnya pecahan berat W. Nilai kekerasan yang tinggi iaitu diantara 119-234 Hv telah diperolehi berbanding W-kuprum komposisi yang sama iaitu 154-182 Hv. kadar haus yang sangat rendah dalam lingkungan 0.002-0.01 mm³ / m turut diperolehi. Kekuatan tegangan komposit dicatatkan pada 89-130 MPa. Selepas 35 hari rendaman didalam air laut, kadar kakisan 0.81-0.52 mm / tahun telah diperolehi bagi sampel yang diterima manakala sampel yang mengandungi Ferum pengaktif mencatatkan rintangan kakisan yang lebih baik (0.10-0.11 mm / thn). Nilai pekali pengembangan haba berada dalam lingkungan 7.40-13.89 x 10⁻⁶ / °C manakala W-kuprum yang digunakan dalam pakej elektronik adalah antara 6.5-8.5 x 10⁻⁶ / °C. Kekonduksian elektrik iaitu 18.45-27.37 % IACS telah diperolehi berbanding 26.77 % IACS yang merupakan standard kebangsaan bagi komposit W-kuprum dengan 47 wt. % W. Selain itu, hasil kajian juga menunjukkan penambahan pengaktif turut menyebabkan kemerosotan kekonduksian elektrik bagi komposit ini. Kesimpulannya, komposit W-loyang yang mempunyai kepadatan tinggi menghampiri ketumpatan teori, sifat mekanik, rintangan kakisan dan ciri-ciri fizikal yang baik telah berjaya dihasilkan

Fabrication and Characterization of Tungsten-brass Composites using Powder Metallurgy process

ABSTRACT

W-Cu composite has been in use for the production of ammunitions, electrode materials for electric discharge machining (EDM), electrical contacts, microelectronic packages, weight balancing in space crafts and in sport vehicles. W-brass composite is a cheaper and an alternative candidate material for the above applications due to its lower sintering temperatures and lower cost of brass than that of Cu. This research was conducted with the main objective of densification of W-brass up to or closer to the theoretical density in order to produce a novel material that could be an alternative to W-Cu composites. The study revealed that conventional solid state and liquid phase sintering cannot be used for the densification of W-brass composites due to mutual insolubility between W, Cu and Zn, compact expansion, dezincification and poor wettability of W by liquid brass. The problem of poor densification was solved by mechanical alloying, direct infiltration and infiltration by shell-on-core. The powders were compacted into 10mm diameter and 3 to 4mm height green compacts. These green compacts were sintered at the temperature of 800 °C, 920 °C, 1000 °C 1150 °C under pure hydrogen atmosphere for 1 – 2 hours. Both pre-mixed and pre-alloyed compacts were subjected to different heating and cooling rates. The mechanical alloying was carried out for 4, 5, 8, 10, 12, 13 and 15 h for the pre-mixed and pre-alloyed powders under pure argon atmosphere. The sintered compacts were tested for density, hardness, tensile strength, wear resistance, corrosion resistance, electrical conductivity and coefficient of thermal expansion. These processes of direct infiltration, infiltration by shell-on-core and mechanical alloying resulted in higher sintered density of up to 99% TD. The hardness of this composite increase as the weight fraction of W increases. High hardness values ranging from 119-234 Hv were obtained compared to 154-182 Hv obtained in W-Cu of the same composition. A very low wear rate in the range of 0.002-0.01 mm³/m was obtained. The tensile strength of the composite is within 89-130 MPa. After 35 days immersion in sea water, the corrosion rate of 0.81-0.52 mm/yr was obtained in the as received samples while the samples containing Fe activator had better corrosion resistance (0.10-0.11 mm/yr). The CTE values are within 7.40-13.89 x 10⁻⁶/°C while that of W-Cu used in electronic packages ranges from 6.5-8.5 x 10⁻⁶/°C. The electrical conductivity of 18.45-27.37% IACS was obtained, compared to 26.77% IACS which is the national standard for W-Cu composite with 47 wt. % W. It was discovered that the addition of an activator deteriorates the electrical conductivity of this composite. In conclusion, W-brass composite with high density closer to the theoretical density, good mechanical properties, corrosion resistance and physical properties was produced.

CHAPTER 1

INTRODUCTION

Metal matrix composites (MMC) are materials that consist of at least two constituents, and with at least one made of metal, while the other one(s) can be different metal, ceramic, or other material(s). If the MMC consists of three or more constituents, it is called a hybrid composite (Yoseph, 2014). An example of MMC is tungsten-copper (W-Cu) composite. W-Cu composite (a pseudo alloy) contains mainly pure tungsten as the principal phase in conjunction with a binder phase comprising of transition metals (Cu, Ni, Fe, Co or Pd) (A Mondal, Agrawal, & Upadhyaya, 2008).

In the past few decades, a lot of researches have been done on W-Cu MMC because of their unique physical and mechanical properties. Their high strength, good fracture toughness, high density, wear resistance and high hardness, make them very useful in military and industrial applications (Kahtan S. Mohammed, Rahmat, & Aziz, 2013). They have found a wide application in the field such as electrical contact, electrodes for spark erosion, shielding materials for microwave packages, nuclear power plants and heat sinks for high power integrated circuits (ICs), because of their high electrical and thermal conductivities, low contact resistance and low thermal expansion coefficients (Kwon et al., 2007; K. S. Mohammed, 2010; Tsakiris et al., 2014; C. Wang et al., 2013). As a result of high melting point of W (3410 °C) and immiscibility in melted copper, it is not possible to use conventional casting methods to produce W-Cu composites (Daneshjou & Ahmadi, 2006; Elsayed et al., 2015; A Upadhyaya & Ghosh, 2002) Thus, W-Cu composites are mainly manufactured through powder metallurgy technology. The idea is to produce a porosity free structure which is a highly recommended feature in any conventional sintering process. Pores in the

microstructures negatively affect thermal and electrical conductivity, and flexural strength of the composite.

Even though a lot of researches and publications have been carried out on the densification of W-Cu systems, no literature is available on the W - brass system. This might be because; zinc is notorious, causing dezincification of its alloys in the sintering process. Brass is an alloy of copper and zinc, usually with zinc as the main additive. The brass used in this research is alpha brass. Alpha brass is typically 70 wt. % copper and 30 wt. % zinc. Alpha brass is an alpha solid solution of zinc in copper. Brass has high malleability than bronze or zinc, low melting temperature which ranges from 900-957 °C and easy to cast because of its high flowability. For the sake of this study, the brass is denoted by br for simplicity.

The most common methods for the fabrication of W-Cu composites are infiltration and liquid phase sintering of the cold-pressed mixture of W and Cu powder (Amirjan, Zangeneh-Madar, & Parvin, 2009; Duan, Lin, Wang, & Yang, 2014; Elsayed et al., 2015; Fan, Liu, Zhu, & Han, 2012; L.-M. Luo et al., 2014; Shu-dong et al., 2009; Xu et al., 2014). Generally, the composite produced by infiltrating the tungsten powder skeleton with the liquid copper yields more superior properties than that by press and sintering the mixture of tungsten and copper (Hiraoka, Inoue, Hanado, & Akiyoshi, 2005). Other methods include powder injection moulding, hot extrusion, spark plasma sintering, mechano-chemical press, field assisted sintering, mechanical alloying and vacuum plasma spray (Gu, 2015; Roosta, Baharvandi, & Abdizade, 2012; Shu-dong et al., 2009). W and Cu exhibit mutual insolubility which makes it very difficult to achieve full densification via liquid phase sintering (A Mondal, Upadhyaya, & Agrawal, 2010). It has been discovered that high sintered density and thermal conductivity are difficult to obtain by common sintering techniques. For improved thermal and mechanical

properties to be achieved, high relative sintered density, high powder purity, particle size reduction and fine homogeneous microstructures are key (Hong SH, 2003; A. Ibrahim, Abdallah, Mostafa, & Hegazy, 2009).

Pre-alloyed brass melts over a range of temperatures. For a brass of 33% Zn, liquid phase starts forming at 902 °C and above (Smallman & Ngan, 1995). On the other hand, in W-Cu system, liquid phase sintering is carried out at temperatures higher than the melting point of copper (1083 °C). Composite materials are well known for the mutual benefits of different properties of non-identical materials. As a result of unique combination of the high thermal and electrical conductivities of copper and the low coefficient of thermal expansion (CTE), high melting point, high hardness, low vapour pressure and high arc erosion resistance of tungsten, these elements are very good candidates for the production of composites having suitable thermo-electrical and arc resistance properties (Abu-Oqail, Ghanim, El-Sheikh, & El-Nikhaily, 2012; Gu D, 2009; Wengel G). Apart from W-Cu, other potential materials for similar applications are Al₂O₃-Cu, Mo-Ag, W-Ag and CdO-Ag (Maji, Dube, & Basu, 2009)

1.1 Tungsten-brass Composites

Tungsten-brass composites are useful in applications where thermal and electrical properties of brass (br) and lower expansion characteristics and high melting temperatures of tungsten can be utilized advantageously. The main areas of applications of these composites are high voltage electrical contacts, kinetic energy penetrators (KEP), a replacement for lead shot which was banned for hunting waterbirds and shooting sports in many countries due to lead poisoning, ammunitions, weight balance in air crafts and sport vehicles, radiation shields, resistance welding electrodes and electro-discharge machining.

The fabrication of W-brass is extremely difficult in both solid and liquid phase sintering. This is because of compacts expansion during sintering, evaporation of zinc (dezincification), the mutual insolubility between W and Cu, and high melting point of W as compared with that of Cu (Amirjan et al., 2009; A Mondal et al., 2010; Shu-dong et al., 2009). In solving densification problems of W-Cu composites, researchers tried different techniques. These techniques include; using fine elemental powders, sintering at higher temperatures, mechanical alloying, coating of W, addition of sintering activators like Fe, Ni, Co and Pd, and increased powder purity (Ahangarkani, Borgi, Abbaszadeh, Rahmani, & Zangeneh-Madar, 2012; Avijit Mondal, Upadhyaya, & Agrawal, 2013). High-energy milling can promote mechanical alloying. Powder fracturing during MA introduces defects into the powder and generates new clean surfaces that are beneficial for atomic diffusion (Mahani Yusoff, 2011). The second most widely used technique after liquid phase sintering is infiltration. In this production route, tungsten skeleton with enough relative density suitable for infiltration is compacted and sintered, and then, molten copper is infiltrated into the open pores of the tungsten porous structure (Duan et al., 2014).

1.2 Importance of the Study

W-brass composite is a candidate material for both military and industrial applications. However, as a result of environmental concern due to lead poisoning, the use of lead in ammunitions has been banned in many countries. The use of lead in ammunition is due to its high density that produces a desirable ballistic performance. W-brass equally has a high density that matches or higher than that of lead, depending on the composition. This composite can be used as an electrode material for electric discharge machining (EDM), electrical contacts and microelectronic packages where optimal electrical conductivity and thermal expansion are desirable. W-brass is better

than W-Cu for some applications such as ammunition, penetrators and anti wear applications. It is equally cheaper to produce due to its lower sintering temperature compared to W-Cu and the cost of brass is about 21% lower than that of copper.

In an attempt to produce an alternative to lead ammunitions and solving the problem of densification of W-Cu composite as an alternative that is equally used in microelectronic packaging, electrodes and electrical contact materials, several research works have been done over the years. Despite the numerous works done by researchers in this field, before now, to be best of my knowledge, no literature is available on W-brass composite. This might be due to its strategic applications for military purposes and the difficulty in sintering components that contain zinc.

1.3 Problem Statement

The densification of W-brass composites has proved to be very difficult for the following reasons:

1. Mutual insolubility of the W, Cu and Zn in both solid and liquid phases.
2. Dezincification, which is the evaporation of zinc above 650 °C.
3. Poor wettability of W by the liquid brass.
4. High differences in the melting point, elasticity modulus and thermal expansion coefficient and compact expansion.

The proposed solutions for the above problems include the use of mechanical alloying (MA) to reduce the particle size, diffusion distance and increase the diffusion rate. Infiltration of the liquid brass to fill the pores created by the evaporation of zinc and the use of shell-on-core which utilizes the difference between the coefficient of thermal expansion W-brass compacts and brass shell are other proposed solutions.

1.4 Objective of the Study

The objectives of this work are;

1. To study the effects of Ni and Fe transition element addition, as sintering activators on the densification and microstructure of W-brass pre-mixed and pre-alloyed composites.
2. To study the effects of the main sintering parameters, such as sintering temperature and time on the densification of different pre-mixed and pre-alloyed W-brass composites.
3. To investigate the effects of mechanically activated sintering (mechanical alloying) on the densification of W-brass composites.
4. To study the densification of W-brass by infiltration technique.
5. To examine a densification technique based on the differences in the coefficient of thermal expansion between W-brass and the brass component to induce compressive stresses that help in enhancing densification.
6. To carry out microstructural, physical and mechanical characterization on both pre-mixed and pre-alloyed sintered samples.

1.5 Scope of the Study

In this study, six main sintering techniques were employed. The main goal of adopting these sintering techniques is to improve the densification leading to fully dense or near fully dense homogeneous structure of W-brass composites. The application of a new approach and sintering concept lead to high density composite and porosity free fully dense structure.

These six techniques are;

- i. Solid state sintering below the melting temperature of brass.
- ii. Super-solidus liquid phase sintering, at the temperature between the solidus and liquidus temperature of brass.
- iii. Liquid phase sintering, which is above the brass melting temperature.
- iv. Powder activation process by mechanical alloying. The milling was in two stages to coat the W with Ni first to avoid the complete solubility of Ni in brass and to enhance the reaction affinity of W with the brass matrix.
- v. Direct infiltration (DI) of the cold compacted W-brass with liquid brass during the sintering process.
- vi. Shell-on-core densification technique, utilizing the difference in the coefficient of thermal expansion (CTE) between hard W phase and the brass matrix as the driving force for densification process.

The secondary goal is to characterize and assess the suitability of the sintered composites for various industrial applications. These assessments include; the tensile strength determined via the Brazilian test, hardness and wear resistance, measuring the physical properties such as the coefficient of thermal expansion and the electrical conductivity. Also, the corrosion rate of the sintered composite was assessed by the immersion corrosion test.