



Ain Shams University
Faculty of Engineering
Design and Production Engineering

The impact of recycling process for tungsten cemented carbide Products by using powder metallurgy technique

A Thesis submitted in partial fulfillment of the requirements of the degree of
Master of Science in Mechanical Engineering
(Design and Production Engineering)

By

Ahmed Osama Abd.El-Aleem Abd.El-Mawla

Bachelor of Science in Mechanical Engineering
(Design and Production Engineering)

Faculty of Engineering, Modern Academy for Engineering and Technology,
2011

Supervised By

Prof. Dr. Mohamed Ahmed Taha

Professor of Design and Production Engineering Department
Faculty of Engineering, Ain Shams University

Assoc. Prof. Dr. OmaymaAbd EL GawadElkady

Head of Powder Technology Division,
Central Metallurgical R&D Institute (CMRDI)

Dr. Ayman Hamada Abd El-Hady

Researcher at Powder Technology Division,
Central Metallurgical R&D Institute (CMRDI)

Cairo – (May.2019)



Ain Shams University
Faculty of Engineering
Design and Production Department

**The impact of recycling process for tungsten cemented
carbide Products by using powder metallurgy technique**

By

Ahmed Osama Abd.El-Aleem Abd.El-Mawla

Bachelor of Science in Materials Engineering

Faculty of Engineering, Modern Academy for Engineering and Technology,
2011

Supervising Committee

Name

Signature

Prof. Dr. Mohamed Ahmed Taha

.....

Ass.Prof. Omayma Abd EL-Gawad Elkady

.....

Dr . Ayman Hamada Abd El.Hady

.....

Date: May.2019

Ain Shams University
Faculty of Engineering
Design and Production Department

**The impact of recycling process for tungsten cemented
carbide Products by using powder metallurgy technique**

by

Ahmed Osama Abd.El-Aleem Abd.El-Mawla

Bachelor of Science In Mechanical Engineering

(Design and Production Engineering)

Faculty of Engineering, Modern Academy for Engineering and Technology, 2011

Examiners´ Committee

Name	Signature
Prof. Dr. Mohamed Ahmed Taha Design and Production, Ain Shams University
Ass.Prof.Dr. Omayma Abd EL-Gawad Elkady Central Metallurgical for R&D Institute (CMRDI)
Prof. Dr. Ahmed Mohamed Mounib Design and Production, Ain Shams University
Prof. Dr. Wafaa Abd-Elraof Metwally Central Metallurgical for R&D Institute (CMRDI)

Date: 2019

Statement

This thesis is submitted as a partial fulfilment of Master of Science degree in Mechanical Engineering, Faculty of Engineering, Ain shams University.

The work included in this thesis was carried out by the author during the 2019, and no part of it has been submitted for a degree or qualification at any other scientific entity.

The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to the work of others.

Signature

Ahmed Osama Abd.El-Aleem Abd.El-Mawla

Date: May.2019

Researcher Data

Name : Ahmed Osama Abd. El-Aleem--
Abd. El-Mawlaa

Date of birth : 11.04.1989

Place of birth : Cairo

Last academic degree : B.Sc. in Mechanical Engineering

Field of specialization : Design and Production Engineering

University issued the degree : Modern Academy for Engineering and
Technology, 2011

Date of issued degree : 2011

Current job : Research Assistant in Central
Metallurgical R&D Institute
(CMRDI).

Dedication

This work is dedicated to the loving memory of my late father, **Mr Osama Abd.el-Aleem**, my mother **Dr. Riri Fawzy**, my two sisters **Amira** and **Ebtihal**, and to all my friends, who supported me throughout my years of study.

Acknowledgements

First of all I would like to express my deepest thanks for almighty ALLAH. I would like to present my thanks and gratitude to my supervisors, **Prof. Dr. Mohamed Ahmed Taha , Assoc. Prof. Dr. Omayma Abd El Gawad Elkady, and Dr . Ayman Hamada Abd El.Hady**, for their intensive supervision, continuous encouragement, valuable discussion and continuous guidance during the research work of the present thesis.

Abstract

Recycling of cemented carbides or hard metals is attracting considerable interest worldwide because of their superior mechanical and physical properties. This work discusses manufacturing of tungsten carbide cutting materials from both fresh powders and recycled ones. As received powder with nominal chemical composition of WC-9% Co-6% TiC-1% TaC- 1%NbC is used for preparing cutting tools. Various compaction pressures from 250 to 730 MPa and sintering temperatures from 1350 to 1450 °C were used in the study. The density, hardness and fracture toughness were measured for all sintered samples. The highest relative density and hardness values are 98% and 1710 HV30, respectively for the sample compacted at 730 MPa and sintered at 1450 °C, while the highest value of fracture toughness is 11.657 MPa.m^{1/2} for the sample compacted at 460 MPa and sintered at 1350 °C. Statistical analysis showed that the most suitable compaction pressure and sintering temperature are 460 MPa and 1400 °C, respectively. The prepared samples are recycled by zinc melt method and the best ratio of zinc to carbide is 1.4:1, which has the highest efficiency of recycled powders (91.55-97.28 %). The recycled WC powder is mixed with the fresh one by 10, 20, 30...and 100 wt. % and is used to manufacture new samples. Results have shown that 70wt.% recycled powder is the optimal mixing composition.

Keywords: Tungsten Carbide, Cobalt binder, Recycling of WC, Sintering process, Compaction, Zinc melt technique.

Summary

Recycling of cemented carbides or hard metals is attracting considerable interest worldwide because of their superior mechanical and physical properties. This study sought to discuss the subjects of manufacturing tungsten carbide from a mixture of fresh powder and recycled one.

As received fresh powder with nominal chemical composition of WC-9% Co-6% TiC-1% TaC- and 1%NbC of 98.66% purity and (2-5) μm particle size, is used for preparing fresh samples. The samples are fabricated by powder metallurgy (PM) technique, in which the powder is milled by using SPEX CertiPrep 8000-series mill for 2 hrs with a ball to powder weight ratio of 5:1 for homogenization of the composition and to reduce their particle size. Milled powder is mixed with 1 wt. % paraffin wax as a lubricant to reduce the friction during compaction process. The powder is then cold pressed at room temperature under various cold compaction pressures ranging from 250 to 730 MPa to study the effect of compaction pressure on compressibility of the fresh powder. The green compacts are then sintered at three temperatures of 1350, 1400, and 1450 $^{\circ}\text{C}$ in vacuum furnace with the heating rate of 5 $^{\circ}\text{C}/\text{min}$ and 1 hour holding time. Microstructure investigation for all samples is performed using both field emission scanning electron microscope (FE-SEM) and optical microscope. The relative densities of the sintered samples are measured by using Archimedes rule. The hardness values of the investigated materials are measured as an average of 5 readings along the cross section surface of the specimens using Vickers hardness test. The fracture toughness is estimated for all sintered samples by using FE-SEM by measuring the cracks length after indentation of the hardness. The results indicated that the highest

relative density and hardness values are 98% and 1710 HV₃₀, respectively for the sample compacted at 730 MPa and sintered at 1450 °C, while the highest value of fracture toughness is 11.657 MPa.m^{1/2} for the sample compacted at 460 MPa and sintered at 1350 °C. Thus, the hardness increased by increasing the sintering temperature, while the fracture toughness decreased. Statistical analysis using JMP software is used for analyzing all the results of fresh samples to find out the suitable conditions of the compaction pressure and sintering temperatures which give the best hardness with the toughness. The analysis showed that the most suitable compaction pressure and sintering temperature are 460 MPa and 1400 °C, respectively.

A group of the prepared samples are then used for recycling process using zinc melt method (ZMM) with different weight ratios of zinc to samples varying from 1:1 to 1.8:1. Samples are potted together in a crucible made from ceramic material (aluminum silicate). The recycling process is performed via sequential steps, which included heating the crucible carrying samples and zinc mixture in muffle furnace at a temperature of 950 °C with 3 h holding time, then vacuum furnace followed by tube furnace, which are used for removing the impurities of zinc. The results showed that the recycling process could yield no contamination of zinc in the recovered WC powder. The results also indicated that the best ratio of zinc metal to carbide samples is 1.4:1, which has the highest efficiency of about (91.55-97.28 %) while obtaining finer particles than the fresh ones. The x-ray fluorescence (XRF), carbon/sulfur analysis (C/S), x-ray diffraction, and field emission scanning electron microscopy are used for characterization of the recycled powder. The recycled WC powder is then mixed with the fresh one by 10, 20, 30... and 100 wt. % and is used to manufacture new samples. The optimized conditions of manufacturing fresh samples are then used to manufacture the recycled samples. Results have shown that 70 wt. %

recycled powder is the optimal mixing composition which showed a good performance of the recycled samples similar to, and even, in some cases, better than, the fresh samples.

List of Contents

Dedication	i
Acknowledgement	ii
Abstract	iii
Summary	iv
List of Contents	vii
List of Figures	x
List of Tables	xiii
List of Abbreviation	xiv
List of Symbols	xv
1. Introduction	1
2. Literature Review	3
2.1. Introduction to Tungsten carbide WC	3
2.2. Classification of WC-Co	4
2.2.1. Un-Alloyed Grades	4
2.2.2. Alloyed Grades	5
2.3. Powder Metallurgy Technique for Composite Production	5
2.3.1. Powder Metallurgy Definition	5
2.3.2. Advantages of Powder Metallurgy	5
2.4.- Factors Affecting the Properties of Tungsten Carbides	6
2.4.1. Compaction of Metal Powders	6
2.4.2. Sintering of the Compacted Samples	10
2.4.3. Grain size of Tungsten Carbide and Cobalt Contents	12
2.5. Recycling of Cemented Carbides	12
2.5.1. Definition of Recycle	12
2.5.2. Benefits of Applying Recycle	13

2.6. Methods For Recycling Cemented Carbide	14
2.6.1. Indirect Recycling Method	14
2.6.2. Semi-Direct Recycling Method	16
2.6.3. Direct Recycling Method	16
2.6.3.1. Cold Stream Process	17
2.6.3.2. Bloating /Crushing Process	17
2.6.3.3. Zinc Melt Method (ZMM)	17
3. Experimental Work	19
3.1. Materials	19
3.2. Experimental Work Flow Chart	20
3.3. Fresh Powders Processing	20
3.3.1. Milling of Fresh Powders	20
3.3.2. Powder Compaction	22
3.2.3. Sintering Process	23
3.3. Fresh Sintered Samples Characterization	25
3.3.1. Relative Density Measurements and Volume Shrinkage Ratio for Sintered Fresh Samples	25
3.3.2. Metallographic Investigation	26
3.3.3. Hardness Measurements	27
3.3.4. Fracture Toughness Test	28
3.3.5. Chemical Composition Analysis	30
3.4. Recycling of Fresh Samples	30
3.4.1. Auxiliary Components for Zinc Melt Methods	30
3.4.2. Sequence of Zinc Melts Process	32
3.5. Preparation of Samples from Recycled Powder with The As-Received Powders	33
4. Results and Discussion	36
4.1. Characterization of Fresh Powders	36

4.1.1. X-Ray Diffraction (XRD) Investigation	36
4.1.2. Microstructure by Field Emission Scan Electron Microscope (FE -SEM)	37
4.1.3. X-Ray Fluorescence (XRF) and Carbon / Sulphur (C/S) Analysis For Fresh Powders	37
4.2. Characterization of The Sintered WC-TiC-Co Samples	39
4.2.1. Phase Analysis and Identification by XRD	39
4.2.2. Microstructure of the Prepared Samples	39
4.2.3. Physical Properties of WC-TiC-Co Composites	45
4.2.3.1. The Green Density of The Compacted Samples	45
4.2.3.2. The Volume Shrinkage of The Sintered Samples	46
4.2.3.3. The Relative Density of The Sintered Samples	47
4.2.4. Mechanical Properties of The Sintered Samples	48
4.2.4.1. Hardness Measurement	48
4.2.4.2. Fracture Toughness	49
4.3. JMP Analysis Results	51
4.4. Recycling of The Sintered WC-TiC-Co Samples	52
4.5. Preparation of New Samples From Recycled WC Powder With The Fresh Ones	54
4.5.1. Microstructure of The Prepared Samples	54
4.5.2. Density Measurement of Sintered Samples	56
4.5.3. Vicker Hardness Measurement of Sintered Samples	56
5. Conclusion	59
References	61
Appendix	
Appendix A : JMP Analysis Definition	69
Appendix B : Phases of the Sintering WC Samples	74
المخلص	1

List of Figures

Figure 2.1	The main powder metallurgy operations steps	6
Figure 2.2	A simplified view of the stages of metal powder compaction	7
Figure 2.3	A flow chart of the compaction process	7
Figure 2.4	effects of increasing green density on densification	8
Figure 2.5	the effect of lubricant content on the density	9
Figure 2.6	stages of the sintering process	10
Figure 2.7	effects of grain size and cobalt contents on mechanical properties of tungsten carbide	12
Figure 2.8	Percentage of tungsten recycling in USA during past years	14
Figure 3.1	FE - SEM graphs for a) fresh powder, b) cobalt powder	19
Figure 3.2	Flow chart of experiment of work.	20
Figure 3.3	Milling machine	21
Figure 3.4	Vials made from stainless steel, all dimension in [mm]	21
Figure 3.5	Uni-axial manual hydraulic press	22
Figure 3.6	The Vacuum Furnace Used For The Sintering Process.	24
Figure 3.7	thermal heating cycle for fresh specimens	24
Figure 3.8	Electronic balance equipped with density measurement device	26
Figure 3.9	Grinding and polishing machine	27
Figure 3.10	Field emission – SEM instrument	28
Figure 3.11	Vickers hardness device	28
Figure 3.12	Geometry of both palmqvist and median cracks	29