

Preparation and Characterization of Some Composites Based on Metals and Ceramics by Mechanical Alloying

A Thesis Submitted to Faculty Collage of Women for Arts, Science, and Education- Ain Shams University

For the Ph. D. Degree in Solid State Physics
By
Mohamed Abdel Aziz Taha Masoud
M. Sc. Solid State Physics

Supervision Committee

Prof. Dr. Hamdia Abd El-Hamid Zayed

Prof. of Solid State Physics
Physics Department
University Collage of Women for Arts,
Science, and Education
Ain Shams University

Dr. Raghieba Abdel Wahab Esawey

Assoc. Prof. of Solid State Physics Solid State Department Physics Division National Research Center

Prof. Dr. Mahmoud Farag Mahmoud Zawrah

Prof. of Chemistry of Advanced Materials &Nanotechnology Ceramic Department Chemical Industrias &Mineral Resources Division National Research Center

Dr. Amira Hassan Abdel Fattah Nassar

Researcher of Solid State Physics Solid State Department Physics Division National Research Center

2013



Preparation and Characterization of Some Composite Based on Metals and Ceramic by Mechanical Alloying.

THESIS SUBMITTED FOR THE Ph. D. DEGREE IN SOLID STATE PHYSICS

By Mohamed Abdel Aziz Taha Masoud

Supervision Committee

Prof. Dr. Hamdia Abd El-Hamid Zayed

Prof. of Solid State Physics
Physics Department
University Collage of Women for Arts,
Science, and Education
Ain Shams University

Dr. Raghieba Abdel Wahab Esawey

Assoc. Prof. of Solid State Physics Solid State Department Physics Division National Research Center

Prof. Dr. Mahmoud Farag Mahmoud Zawrah

Prof. Chemistry of Advanced Materials
&Nanotechnology
Ceramic Department
Chemical Industrias &Mineral Resources
Division
National Research Center

Dr. Amira Hassan Abdel Fattah Nassar

Researcher of Solid State Physics Solid State Department Physics Division National Research Center

Date of Research: / / 2013

Approval Stamp: Date of Approval: // 2013

Approval of Faculty Council. Approval of University Council.

Mohamed Abdel Aziz Taha Masoud NAME OF STUDENT: TITLE OF THESIS: **Preparation and Characterization of** Some Composites Based on Metals and Ceramic by Mechanical Alloying. **SCIENTIFIC DEGREE: DOCTOR OF PHILOSOPHY** IN PHYSICS (SOLID STATE PHYSICS). **DEPARTMENT: PHYSICS** NAME OF FACULTY: FACULTY COLLAGE OF WOMEN FOR ARTS, SCIENCE, AND EDUCATION. UNIVERSITY AIN SHAMS. **B. SC. GRADUATION DATE:** M. SC. GRADUATION DATE: Ph. D. GRADUATION DATE:

CONTENT

LIST OF FIGURES	I
ACKNOWLEDGEMENTS	v
ABSTRACT	VI
1. Introduction	1
1.1. Nanotechnology	1
1.2. Composites	2
1.2.1. Metal Matrix Composites	3
1.2.1.1. Cu/ Al ₂ O ₃ Nanocomposites	4
1.2.2. Ceramic Matrix Composites	5
1.2.2.1. Al ₂ O ₃ /Cu Nanocomposites	6
2. Theoretical background	7
2.1. Mechanical Alloying	7
2.1.1. Introduction	7
2.1.2. History of Mechanical Alloying	8
2.1.3. History of Nanostructure by Mechanical Alloying	10
2.1.4. Mechanism of Alloying	11
2.1.4.1. Ductile- Ductile system	11
2.1.4.2. Ductile- Brittle system	13
2.1.4.3. Brittle- Brittle system	14
2.1.5. Important Components of Milling	14
2.1.5.1. Raw Materials	14
2.1.5.2. Types of Mills	15
2.1.5.2.1. SPEX Shaker Mills	15
2.1.5.2.2. Planetary Mills	16
2.1.5.2.3. Attritor Mills	16
2.1.5.3. Process Variables	17

		2.1.5.3.1. Milling Speed and Time	17
		2.1.5.3.2. Milling Medium	18
		2.1.5.3.3. Ball-to-Powder Weight Ratio	18
		2.1.5.3.4. Process Control Agent	19
	2.2.	Consolidification	- 19
	2.2	2.1. Compaction	- 19
		2.2.1.1. Die Compaction	- 20
	2.2	2.2. Sintering	- 21
		2.2.2.1. Type of Sintering	- 23
		2.2.2.2. Sintering Atmosphere	- 24
		2.2.2.3. Process Variables	- 25
	2.3.	X- ray Diffraction	26
	2.4.	Mechanical Properties	27
	2.4	4.1. Hardness	27
	2.4	4.2. Fracture Toughness	28
	2.5.	AC electrical conductivity	32
	2.5	5.1. Models of AC conductivity	32
3.	Liter	rature Review	- 37
	3.1.	Cu/ Al ₂ O ₃ Composites	- 37
	3.2.	Al ₂ O ₃ /Cu Composites	- 41
4.	Mate	erial and Experimental Processes	- 46
	4.1.	Raw Materials	- 46
	4.2.	Powder synthesis by Mechanical Alloying	- 46
	4.3.	Characterization of Structure Analysis	48
	4.3	3.1. Structure analysis	48
	4.3	3.2. 3.3.2. Morphology and Particle Size of the Synthesized Powders	- 49
	4.4.	Consolidification of Synthesized Composites	49

	4.5.	Relative Density and Apparent Porosity	- 50
	4.6.	Mictostructure of the Sintered Composites	51
	4.7.	Mechanical Properties of the Sintered Composites	52
	4.7	.1. Vicker Hardness	52
	4.7	.2. Fracture Toughness	- 52
	4.8.	AC Electrical Conductivity	- 53
5.	Resu	lts and Discussion	- 55
	5.1.	Cu Matrix Composites	55
	5.1	.1. Characterization of the Prepared Powders	55
	4	5.1.1.1. Phases Composition of the Prepared Powders	- 55
		5.1.1.1. Lattice Parameters	60
		5.1.1.2. Full Width at High Maximum (FWHM)	63
		5.1.1.3. Crystallite Size and Lattice Strain Measurement	- 66
	4	5.1.1.2. Morphology of the Prepared Powders	70
	5.1	.2. Sinterability of the prepared Nanocomposites	- 81
		5.1.2.1. Relative Density and Apparent Porosity	81
		5.1.2.2. Microstructure and Chemical Composition of the Sintered	
		Composites	- 87
		5.1.2.3. Microhardness of the Sintered Composites	- 95
		5.1.2.4. AC Electrical Conductivity	- 98
	5.2.	$Al_2O_3/Cu\ Composites\$	105
	5.2	.1. Characterization of the Prepared Powders	105
		5.2.1.1. Phases Composition of Prepared Powders	105
		5.2.1.1.1. Lattice Parameters	108
		5.2.1.1.2. Full Width at High Maximum (FWHM)	111
		5.2.1.1.3. Crystallite Size and Lattice Strain Measurement	114
		5.2.1.2. Morphology of the Prepared Powders	117

5.2.2. Sinte	erablity of the Prepared Nanocomposites	127
5.2.2.1.	Relative Density and Apparent Porosity	127
5.2.2.2.	Microstructure and Chemical Composition of the Sintered	
	Composites	- 134
5.2.2.3.	Microhardness and Fracture Toughness of the	
	Sintered Composites	142
5.2.2.4.	AC Electrical Conductivity	146
5. CONCLUSIO	N	152
REFERENCES		155
الملخص العريي		1



LIST OF FIGURES

Figure 2.1	: Amount of publications concerning materials developed by mechanicalloying	cal 10
Figure 2.2:	Various stages of a ductile - ductile system during mechanical alloying	12
Figure 2.3:	Various stages of a ductile - brittle system during mechanical alloying	13
Figure 2.4:	SPEX Certiprep 8000D mixer mill	15
Figure 2.5:	FRITSCH GmbH, planetary mill	16
Figure 2.6:	Attritor GmbH, planetary mill	17
Figure 2.7:	Single and double acting powder compaction	21
Figure.2.8:	XRD basic principle schematic diagram.	26
Figure 2.9:	Vickers Hardness Indenters	28
Figure 2.10	: Palmqvist Cracking System	29
Figure 2.11:	Frequency exponent s as a function of temperature for all mechanisms of conduction3	ac 6
Figure 4.1:	Planetary ball used for mechanical alloying	47
Figure 4.2:	Compaction die set.	49
Figure 4.3:	Block diagram of AC circuit	53
Figure 4.4:	Over all experimental procedures for the present study	54
Figure 5.1:	XRD pattern of as-received pure Copper	55
Figure 5.2:	XRD pattern of as-received pure Alumina	56
Figure 5.3:	XRD pattern of mechanically alloyed; (a) Cu, (b) Cu-1wt.%Al ₂ O ₃ , (c) C 5wt.% Al ₂ O ₃ , (d) Cu-10wt.% Al ₂ O ₃ and Cu-20wt.% Al ₂ O ₃ compos powders at different milling time.	u- ite 57
Figure 5.4:	Lattice parameter at different milling time; (a) Cu, (b) Cu-1wt. % Al_2O_3 , Cu-5wt.% Al_2O_3 , (d) Cu-10wt.% Al_2O_3 and Cu-20wt.% Al_2O_3 compos powders	ite
Figure 5.5:	Full width at half maximum (FWHM) for : (a) Cu, (b) Cu-1wt.% Al_2O_3 , (c) C 5wt.% Al_2O_3 , (d) Cu-10wt.% Al_2O_3 and Cu-20wt.% Al_2O_3 composite powders different milling time	at
Figure 5.6:	Effect of milling time on crystal size and lattice strain for : (a) Cu, (b) C lwt.% Al ₂ O ₃ , (c) Cu-5wt.% Al ₂ O ₃ , (d) Cu-10wt.% Al ₂ O ₃ and Cu-20wt.% Al ₂ composite powders.	O ₃
Figure 5.7:	TEM photomicrograph of pure Cu particle milled at different milling time; 1h, (b) 5h, (c) 10h, (d) 15h and (e) 20h	(a) 71

Figure 5.8:	TEM photomicrographs of Cu-5wt.% Al_2O_3 composite particles milled at different milling, (a) 1h, (b) 5h, (c) 10h, (d) 15h and (e) 20h75
Figure 5.9:	TEM photomicrographs of Cu-20wt.% Al_2O_3 composite particles at different milled, (a) 1h, (b) 5h, (c) 10h, (d) 15h and (e) 20h77
Figure 5.10:	Effect of milling time on particles size of Cu, Cu-5wt.% Al ₂ O ₃ and Cu-20wt.% Al ₂ O ₃ composites 80
Figure 5.11:	Relative density of sintered (a) Cu, (b) Cu-1wt.% Al_2O_3 , (c) Cu-5wt.% Al_2O_3 , (d) Cu-10wt.% Al_2O_3 and Cu-20wt.% Al_2O_3 composites at different both milling time and sintering temperature. ——82
Figure 5.12:	Apparent porosity of sintered (a) Cu, (b) Cu-1wt.% Al_2O_3 , (c) Cu-5wt.% Al_2O_3 , (d) Cu-10wt.% Al_2O_3 and Cu-20wt.% Al_2O_3 composites at different both milling time and sintering temperature84
Figure 5.13:	SEM microphotographs of the sintered Cu-20wt.% Al ₂ O ₃ composite 1h at 850°C and different milling time; (a) 1h, (b) 5h, (c) 10h, (d) 15h and (e) 20h
Figure 5.14:	SEM Microphotograph of sintered: (a) Cu, (b) Cu1wt.% Al ₂ O ₃ , (c) Cu-5wt.% Al ₂ O ₃ , (d) Cu-10wt.% Al ₂ O ₃ composites, at 850°C prepared from powders milled for 20h91
Figure 5.15:	EDX spectra of sintered (a) Cu, (b) Cu-1wt.% Al_2O_3 , (c) Cu-5wt.% Al_2O_3 , (d) Cu-10wt.% Al_2O_3 and (e) Cu-20wt.% Al_2O_3 composites prepared from powders milled for 20h
Figure 5.16	: Effect of milling time on microhardness of Cu and Cu-20wt.% Al_2O_3 composites sintered 1h at 850 °C97
Figure 5.17:	Effect of Al ₂ O ₃ content on microhardness of Cu base composite sintered 1h at 850°C and prepared from powders milled at 20h97
Figure 5.18	AC conductivity in relationship with frequency at room temperature of sintered Cu base composites prepared from powders milled for 20h98
Figure 5.19:	Variations of AC conductivity of Cu-20wt.% Al_2O_3 composites as a function of milling time at room temperature and different frequency100
Figure 5.20	: Variation of AC conductivity, σ_{ac} with frequency, ω at fixed different temperatures and for Cu-20wt% Al ₂ O ₃ composites prepared from milled powders for 20h
Figure 5.21:	Temperature dependence of the AC conductivity, σ_{ac} at different frequencies, ω for Cu-20 wt% Al ₂ O ₃ composite prepared from milled powders for 20 102
Figure 5.22:	Frequency dependence on of AC conduction activation energy for Cu-20wt % Al_2O_3 composites prepared from milled powders for 20h103
Figure 5.23:	Temperature dependence of the frequency exponent "s" for Cu-20 wt% Al ₂ O ₃ composites prepared from milled powders for 20h 104
Figure 5.24:	XRD patterns of mechanically alloyed (a) Al ₂ O ₃ , (b) Al ₂ O ₃ -1wt. %Cu, (c) Al ₂ O ₃ -5wt.%Cu, (d) Al ₂ O ₃ -10wt.%Cu and (e) Al ₂ O ₃ -20wt.%Cu composite powders at different milling time.———————————————105

Figure 5.25:	Lattice parameters at different milling time for; (a) Al_2O_3 , (b) $Al_2O_31wt.\%Cu$, (c) $Al_2O_3-5wt.\%Cu$, (d) $Al_2O_3-10wt.\%Cu$ and (e) $Al_2O_3-20wt.\%Cu$ composite powders
Figure 5.26:	Full width at half maximum (FWHM) for : (a) Al_2O_3 , (b) Al_2O_3 -1wt.%Cu, (c) Al_2O_3 -5wt.%Cu, (d) Al_2O_3 -10wt.%Cu and (e) Al_2O_3 -20wt.%Cu composite powders at different milling time
Figure 5.27:	Effect of milling time on crystallite size and lattice strain of Al_2O_3 , Al_2O_3 -1wt.%Cu, Al_2O_3 -5wt.%Cu, Al_2O_3 -10wt.%Cu and Al_2O_3 -20wt.%Cu composite powders
Figure 5.28:	TEM photomicrographs of Al ₂ O ₃ particles at different milling time, (a) 1h, (b) 5h, (c) 10h, (d) 15h, (e) 20h118
Figure 5.29:	TEM photomicrographs of Al ₂ O ₃ -5wt.% Cu particles at different milling time, (a) 1h, (b) 5h, (c) 10h, (d) 15h, (e) 20h
Figure 5.30:	TEM photomicrographs of Al_2O_3 -20wt.% Cu particles at different milling time, (a) 1h, (b) 5h, (c) 10h, (d) 15h, (e) 20h
Figure 5.31:	Effect of milling time on particles size of Cu, Cu-5wt.% Al ₂ O ₃ and Cu-20wt % Al ₂ O ₃
Figure 5.32:	The relatioship between the relative density, milling time of starting powders and sintring temperature for (a) Al_2O_3 , (b) Al_2O_3 -1wt.%Cu, (c) Al_2O_3 -5wt.%Cu, (d) Al_2O_3 -10wt.%Cu and (e) Al_2O_3 -20wt.%Cu composites128
Figure 5.33	The relatioship between the apparent porousity, milling time of starting powders and sintring temperature for (a) Al_2O_3 , (b) Al_2O_3 -1wt.%Cu, (c) Al_2O_3 -5wt.%Cu, (d) Al_2O_3 -10wt.%Cu and (e) Al_2O_3 -20wt.%Cu composites.
	131
Figure 5.34:	SEM Microphotographs of the sintered Al ₂ O ₃ -20wt.%Cu composite at 1550 °C for 1h at different milling time. (a) 1h, (b) 5h, (c) 10h, (d) 15 h, and (e) 20h. ————————————————————————————————————
Figure 5.35:	SEM microphotographs of (a) Al_2O_3 , (b) Al_2O_31 wt.%Cu, (c) Al_2O_3 -5wt.%Cu and (d) Al_2O_3 -10wt.%Cu composites sintered at 1550 °C for 1h138
Figure 5.36:	EDX spectra of sintered; (a) Al_2O_3 , (b) Al_2O_31 wt.%Cu, (c) Al_2O_3 -5wt.%Cu and (d) Al_2O_3 -10wt.%Cu composites prepared from powders milled for 20h
	= - 7

•	Microhardness versus milling time for Al ₂ O ₃ & Al ₂ O ₃ -20wt.%Cu composite sintered for 1 h at 1550 °C in argon of starting powder143
	Effect of milling time on fracture toughness of Al ₂ O ₃ & Al ₂ O ₃ -20 wt.% Cu composits sintered 1 h at 1550 °C——————————————————————————————————
Figure 5.39:	Effect of Cu content on microhardness and fracture toughness of Al_2O_3 sintered for 1h at 1550 °C prepared from powder milled for 20h145
Figure 5.40:	SEM microphotograph showing crack propagation on the surface of Al_2O_3 -20wt.%Cu composite sintered for 1h at 1550 °C prepared from powder milled for 20h
Figure 5.41: A	AC conductivity verses frequency at room temperature of sintered Al ₂ O ₃ base composites prepared from powder milled for 20h
Figure 5.42:	Variations of AC conductivity of sintered Al ₂ O ₃ -20 wt.%Cu composites as a function of milling time of starting power and different frequency148
Figure 5.43:	Variation of AC conductivity, σ_{ac} fixed temperature with frequency, ω for Al ₂ O ₃ -20wt%Cu composites prepared from power milled for 20h149
Figure 5.44: 7	Temperature dependence of the AC conductivity at different frequency, $ω$ for Al ₂ O ₃ -20wt %Cu composites prepared from power milled for 20h 150
	Frequency dependence on AC conduction activation energy for Al ₂ O ₃ -20 wt % Cu composites
	Temperature dependence of the frequency exponent "s" for Al ₂ O ₃ -20 wt % Cu composites prepared from milled powders for 20h151

ACKNOWLEDGEMENTS

ACKNOWLEDGEMENTS

- **Ø** All gratitudes are due to <u>Allah</u> who guided and showed me the right path, without his help my efforts would have gone astray.
- I would like to thank, <u>Prof. Dr. Hamdia Abd El-Hamid Zayed</u>, Prof. of Solid state physics, Physics department, in University Collage of Women for Arts, Science, and Education, Ain Shams University for her supervision, guidance and advising me in all times. I am grateful for her enthusiasm and encouragement that she has given me.
- Deepest thanks and sincere gratitude to <u>Dr. Raghieba Abdel Wahab Esawey</u>, Assoc. prof. of Solid State Physics, National Research Center, Physics Division, Solid State Physics Department, for his supervision and fruitful discussion as well as I am grateful for his assistance, advice and guidace for choosing the research point.
- Special thanks for <u>Prof. Dr. Mahmoud Farag Mahmoud Zawrah</u>, Prof. of Advanced Materials and Nanotechnology, Ceramic Research Department, National Research Center, for suggesting the point of research, supervision, fruitful discussion as well as I am grateful for his assistance, advice
- **Ø** Also Great thanks for <u>Dr. Amira Hassan Abdel Fattah Nassar</u>, Researcher of Solid State Physics, National Research Center for her supporting, guiding, and advising me in all times.

ABSTRACT