THE EFFECT OF AGING TREATMENT ON THE MICROSTRUCTURE AND THERMODYNAMIC PARAMETERS OF CUAINi -Mn SHAPE MEMORY ALLOYS (SMAs)

ALI ABED SHAKIR

UNIVERSITI TEKNOLOGI MALAYSIA

THE EFFECT OF AGING TREATMENT ON THE MICROSTRUCTURE AND THERMODYNAMIC PARAMETERS OF CUAINi -Mn SHAPE MEMORY ALLOYS (SMAs)

ALI ABED SHAKIR

A project report submitted in partial fulfillment of the requirements for the award of the degree of Master of Engineering (Mechanical-Materials)

> Faculty of Mechanical Engineering Universiti Teknologi Malaysia

> > JANUARY 2014

This project report is dedicated to my beloved mother, brothers and sisters, for their endless support and encouragement.

ACKNOWLEDGEMENT

I would like to express my gratefulness to all entities that are involved in my project work. In preparing this project, I was in contact with many people, researchers, academicians and technicians. They all have contributed to my understanding and valuable thoughts during my project.

First and foremost, I wish to express my sincere appreciation to my supervisor, Dr. Tuty Asma Abu Bakar for encouragement, guidance and critics. Their kindness and encouragement helped me to persevere along the way. Without their continued support and advices, this thesis would not have been the same.

Last but not least, I am grateful to my **mother**, **sisters** and **brothers**, **Muslim**, **Aqeel** and **Maytham**, and all family members for their moral and financial support and understanding all this time.

ABSTRACT

This thesis presents the effect of heat treatment on the microstructure and thermodynamic parameters of CuAlNi -Mn SMA. The effects of different aging temperatures of 300°C, 400°C and 500°C at various aging times were evaluated using the optical microscopy, FESEM and the XRD, to investigate their microstructure and phase transformation. The martensite and austenite transformation temperatures of CuAlNi -Mn SMA have been determined by the differential scanning calorimetry (DSC), while the hardness property using Vickers hardness. The variation of the structure and properties of alloy were influenced by the morphology and the type of the phases obtained. The observation revealed that the grain size and the grain boundary of CuAlNi -Mn SMA increase with increasing the aging temperatures and aging times. Due to this, the values of Vickers hardness were observed to decrease at elevated temperatures and prolonged aging times. On the other hand, the changes of thermodynamic parameters were observed with regard to the variation of aging temperatures and aging time. The enthalpy and entropy were observed increase with increasing the aging temperatures and aging times.

ABSTRAK

Tesis ini membentangkan kesan rawatan haba ke atas mikrostruktur dan parameter termodinamik untuk aloi memori bentuk CuAlNi -Mn. Kesan–kesan suhu penuaan yang berbeza iaitu 300°C, 400° dan 500°C pada pelbagai masa penuaan dinilai dengan mikroskop optik, FESEM dan XRD, untuk menyiasat mikrostruktur dan perjelmaan fasa. Suhu penjelmaan fasa austenite dan martensit aloi memori bentuk CuAlNi -Mn ditentukan menggunakan alat DSC, manakala sifat kekerasan menggunakan alat kekerasan Vickers. Kepelbagaian struktur dan sifat aloi ini dipengaruhi oleh morfologi dan jenis fasa yang di hasilkan. Pemerhatian menunjukkan saiz bijian dan sempadan bijian CuAlNi -Mn meningkat dengan peningkatan suhu dan masa penuaan. Ini menyebabkan kekerasan diperhatikan menurun dengan peningkatan suhu dan masa penuaan. Disamping itu, parameter termodinamik turut berubah dengan peningkatan suhu dan masa penuaan. Entalpi dan entropi diperhatikan meningkat dengan peningkatan suhu dan masa penuaan.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	V
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	X
	LIST OF FIGURES	xi

1	INT	RODUCTION	1
	1.1	Background	1
	1.2	Problem Statement	2
	1.3	Objectives	3
	1.4	Scope	3
	1.5	Thesis Organization	4
2	т іт	FRATURE REVIEW	5
4			5
	2.1	Introduction	3
	2.2	Shape Memory Alloys (SMAs)	6
	2.3	Martensitic Transformation of Shape Memory Alloys	6
		(SMAs)	

2.4	Common properties of SMAs	10
	2.4.1 Pseudoelasticity (PE) or Superelasticity (SE)	10
	2.4.2 Shape Memory Effect (SME)	11
2.5	Application of Shape Memory Alloys (SMAs)	13
2.6	Classification of Shape Memory Alloys (SMAs)	14
	2.6.1 Ti-Ni system alloys	14
	2.6.1.1 Shape Memory Properties of NiTi	15
	alloys	
	2.6.1.2 Ti-Ni Phase Diagram	16
	2.6.2 Copper-Based Alloys	17
	2.6.2.1 Cu-Zn-Al Alloy	17
	2.6.2.2 CuAlNi Alloy	18
	2.6.3 Iron-base alloys	19
2.7	CuAlNi Alloys	20
	2.7.1 Phase transformation of CuAlNi alloy	23
	2.7.2 Phase diagram of CuAlNi alloy	25
2.8	Aging of Copper-Based Shape Memory Alloys	26
	2.8.1 Effect of aging treatment on CuAlNi and	29
	CuAlNi -Mn SMAs	
2.9	Effect of aging treatment on thermodynamic	34
	parameter	
RE	SEARCH METHODOLOGY	38
3.1	Introduction	38
3.2	Research Methodology Design	38
3.3	Material	40
3.4	Aging Experiments	40
3.5	Phase and Microstructural Analysis	41
	3.5.1 X-ray Diffraction	41
	3.5.2 Optical Microscopy (OM)	41
	3.5.3 Field Emission Scanning Electron	42
	Microscopy (FESEM)	
3.6	Determination of Phase Transformation Temperatures	43

3

		3.6.11	Differential Scanning Calorimetry (DSC)	43
	3.7	Determ	nination of material hardness	44
		3.7.1	Vickers Hardness Test	44
4	RE	SULTS	AND DISCUSSION	45
	4.1	Introdu	iction	45
	4.2	Chemi	cal Composition Analysis	45
	4.3	Effects	of aging process	50
		4.3.1	Microstructure of CuAlNiMn shape memory	50
			alloys (SMAs)	
		4.3.2	X-ray Diffraction Analysis	67
		4.3.3	Mechanical properties	70
			4.3.3.1 Hardness	70
		4.3.4	Determination of Phase Transformation	73
			Temperatures	
			4.3.4.1 Differential Scanning Calorimetry	73
			(DSC)	
_	~~~			~ -

5	CO	NCLUSIONS	85
	5.1	Conclusions	85
	5.2	Recommendation for future work	86

REFERENCES

87

LIST OF TABLES

TABLE NO

TITLE

PAGE

4.1	The average of grain size before and after aged	57
4.2	Hardness values of CuAlNi -Mn shape memory alloys	71
4.3	The transformation temperature and thermodynamic	80
	parameters of CuAlNi -Mn alloy at 300°C for various	
	aging times	
4.4	The transformation temperature and thermodynamic	80
	parameters of CuAlNi -Mn alloy at 400°C for various	
	aging times	
4.5	The transformation temperature and thermodynamic	
	parameters of CuAlNi -Mn alloy at 500°C for various	
	aging times	

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	Microscopic and Macroscopic Views of the Two	8
	Phases of Shape Memory Alloys	
2.2	Schematic of pseudoelastic stress – strain diagram	9
2.3	Schematic of stress – temperature phase diagram for	9
	an SMA	
2.4	Schematic diagram showing stress-induced	10
	martensitic transformation	
2.5	Schematic representation of the martensite	11
	volume as a function of temperature in	
	martensitic transformation	
2.6	Schematic representation of the microstructural	12
	and macroscopic change of a SMA rod	
	exhibiting SME	
2.7	Ti-Ni phase diagram with enlarged region of	16
	metastable intermetallic	
2.8	The phase diagram showing the vertical cross	18
	section of Cu-Zn-Al ternary systems with fixed 6	
	wt% Al	
2.9	Schematic map of the kind of martensite according	24
	to changing aluminum and nickel contents	
2.10	The phase diagram showing the vertical cross	25
	section of CuAlNi ternary systems with fixed	
	3wt%Ni)	

2.11	DO3 unit cell showing position of atoms	27
2.12	Long Period Stacking Order Structure of 2H	27
	Martensit	
2.13	Long Period Stacking Order Structure of 18R1	28
	Martensite	
2.14	The changes in hardness (A), electrical resistivity	31
	(B) and transformation temperatures (C)	
2.15	Increase in As as a function of aging time for	33
	various quenching temperatures, Tq and aging	
	temperatures, Ta	
2.16	Schematic representation of free energy curves	35
	for both austenite and martensite, and their	
	relation to he Ms and As temperatures.	
2.17	Changes of transformation temperatures with	37
	various aging times in CuAlNi alloy	
3.1	Research methodology designed	39
3.2	Sketch of the heat treatment process	40
3.3	Glazing X-ray Diffractrometer	41
3.4	Nikon (FXL) optical microscope	42
3.5	FESEM equipped with DEX	42
3.6	DSC equipped	43
3.7	Vickers hardness	44
4.1	Chemical Composition of unaged sample by	46
	EDX	
4.2	Chemical Composition of aged samples by EDX	47
	at 300 °C	
4.3	Chemical Composition of aged samples by EDX	48
	at 400 °C	
4.4	Chemical Composition of aged samples by EDX	49
	at 300 °C	
4.5	Optical micrograph of unaged sample of CuAlNi	50
	-Mn (SMAs) Sample	

4.6	Optical micrographs of aged samples of CuAlNi	51
	-Mn (SMAs) at 300 °C and different aging times	
4.7	Optical micrographs of aged samples of CuAlNi	53
	-Mn (SMAs) at 400 °C and different aging times	
4.8	Optical micrographs of aged samples of CuAlNi	55
	-Mn (SMAs) at 500 °C and different aging times	
4.9	Mapping of elements and EDX of CuAlNi -Mn	59
	alloy	
4.10	FESEM of samples of CuAlNi -Mn (SMAs) at	60
	300 °C	
4.11	FESEM of samples of CuAlNi -Mn (SMAs) at	62
	400 °C	
4.12	FESEM of samples of CuAlNi -Mn (SMAs) at	65
	500 °	
4.13	XRD pattern for unaged and aged samples at	69
	300°C	
4.14	XRD pattern for unaged and aged samples at	69
	400°C	
4.15	XRD pattern for unaged and aged samples at	70
	500°C	
4.16	The effect of aging time and aging temperature	72
	on the hardness	
4.17	The effect of aging time and aging temperature	72
	on the grain size	
4.18	DSC result of unaged sample	73
4.19	DSC result of aged samples at 300°C	74
4.20	DSC result of aged samples at 400°C	76
4.21	DSC result of aged samples at 500°C	78
4.22	Changes of transformation temperatures with	82
	various aging times in CuAlNi -Mn alloy	
4.23	Changes of enthalpy and entropy with various	84
	aging times for different aging temperature in	
	CuAlNi -Mn alloy	

CHAPTER 1

INTRODUCTION

1.1 Background

Shape memory alloys (SMAs) are one of the unique classes of smart materials, which have the ability to recover their shape when the temperature is applied. Shape memory alloys (SMAs) can absorb and dissipated the mechanical energy by undergoing a reversible hysteresis shape change when subjected to applied mechanical cyclic load. These unique characteristics of shape memory alloys (SMAs) have made them more suitable to be used of sensing and actuation, impact absorption and vibration, damping applications. Moreover, the functional characteristic of shape memory alloys (SMAs) is largely related to the thermoelastic martensitic transformation, which generally occurs in the 173-473 K temperature range, depending on the alloy composition and heat treatment. These properties are significantly affected by the mobile nature of the interfaces (twin boundaries, martensitic variants, parent/martensite phase boundaries). Among the several alloy systems that exhibit shape memory characteristics, Cu-based SMAs have received a considerable attention because of their high thermal stability. One of the most important Cu-based shape memory alloys are the Cu-Al-Ni, whereas it has a high transformation temperature comparing with other shape memory alloys, that made it

more suitable for works for high temperature applications. There are several literatures and experimental works related to these alloys, whereas they showed that there are two main parameters are mostly affected on the phase transformation behavior, they are the addition of alloying elements and aging treatment. Aging treatment is mainly time- temperature dependent, which can control the redistribution of the materials atoms into the phase structure. The variation of aging times or aging temperatures can cause into the variation microstructure and phases. For the CuAlNi -Mn system, three stages of aging process have been described. In the first stage, the transformation characteristics remain generally stable; sometimes a slight decrease of the transformation temperatures is shown. In the second stage, the transformation temperatures increase whereas progressive deterioration of the shape memory occurs in the third stage hysteresis.

Therefore, the aim of the project is to study the effect of aging treatment on the microstructure and thermodynamic parameter variations of CuAlNi -Mn shape memory alloys (SMAs) at different aging temperatures and aging times.

1.2 Problem Statement

CuAlNi shape memory alloys are loss prone to the stability of the obtaining phase due to the high brittleness that may related to the type and structure of the this phase, that may obtain a limit by the applications of these alloys. To overcome these problems alloying elements have been added to adjust the phase diagram and improve the mechanical properties. This project will concern on finding the changes of the microstructure and thermodynamic parameter of the CuAlNi -Mn SMAs that can cause by varying the aging treatment parameters, such as aging times and aging temperatures.

1.3 Objectives

The project work aimed to fulfill the following objectives:

- To examine the microstructure and phase variations of CuAlNiMn (SMAs) after various aging treatment processes.
- To investigate the effect of different aging treatment temperature and time on the thermodynamic parameters of the obtained phase.

1.4 Scope

- Apply different aging treatment process with varying the aging time and aging temperature (300, 400, and 500) °C for (1, 2, 3, 4, and 5) hrs.
- Use the optical microscope (OM) and scanning electron microscope (SEM) to investigate the effect of aging treatment on microstructure of CuAlNi -Mn Shape memory alloys.
- Use the X-Ray Diffraction (XRD) for obtaining the phase transformation variation after the aging treatments are applied.
- Use the Differential Scanning Calorimetry (DSC) to determine the variation of transformation temperature during the aging treatment (M_s, M_f, A_s, and A_f).
- Use the theoretical calculation to measure the thermodynamic parameters of CuAlNi -Mn SMA under different aging treatment.

1.5 Thesis Organization

This thesis comprises of six chapters. The first chapter is the Introduction. It describes the background of the problem included problem statement, project objectives and project scope. Chapter 2 focuses on Literature Reviews. This chapter highlights the background knowledge on the Shape Memory Alloys (SMAs), Common properties, Classification and application of Shape Memory Alloys (SMAs), and the effect of aging treatment on microstructure ana thermodynamic parameter of CuAlNi and CuAlNi -Mn SMAs. Chapter 3 describes the Methodology used to carry out this project and method to analyze experimental results. Chapter 4 discusses the results that will obtain by X-ray Diffraction, Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Vickers Hardness Test. Chapter 5 presents the conclusion.

REFERENCES

- Otsuka K. and Wayman. C. M. 1998. Shape Memory Material. Cambridge University Press.
- [2] El Feninat F., Laroche, G., Fiset M., and Mantovani D. 2002. Advanced Engineering Materials 4, 9.
- [3] Kennedy J.B., Funakubo H. (Ed.). 1987. Shape Memory Alloys. Gordon and Breach Science Publishers.
- [4] Lagoudas, D. C. (Ed.). 2008. Shape memory alloys: modeling and engineering applications. Springer.
- [5] Nica, Valentin. Structure formation and its effect on properties of shape memory materials.
- [6] Wei, Z. G., Sandstroröm, R., & Miyazaki, S. 1998. Shape-memory materials and hybrid composites for smart systems: Part I Shape-memory materials. *Journal* of Materials Science, 33(15), 3743-3762.
- [7] Paula, A. S. et al. 2004. Effect of thermal cycling on the transformation temperature ranges of a Ni–Ti shape memory alloy. *Materials Science and Engineering: A*, 378(1), 92-96.
- [8] Yeung, K. W. K. et al. 2004. Optimization of thermal treatment parameters to alter austenitic phase transition temperature of NiTi alloy for medical implant. *Materials Science and Engineering: A*, 383 (2), 213-218.
- [9] Zhang, Jian, et al. 2007. Does order-disorder transition exist in nearstoichiometric Ti-Ni shape memory alloys. *Materials Science and Engineering: A.* 55.8, 2897-2905.
- [10] L. Delaey, A. et al. 1978. Shape Memory Effect, Super-Elasticity and Damping in Cu-Zn-Al Alloys. INCRA: 238.

- [11] Wei, Z. G., R. Sandstroröm, and S. Miyazaki. 1998. Shape-Memory Materials and Hybrid Composites for Smart Systems. *Materials Science: A* 33.15, 3743-3762.
- [12] Kneissl, A. C., et al. 2008. Microstructure and Properties of Niti and Cualni Shape Memory Alloys. *Metalurgija*, 14(2), 89-100.
- [13] Wang, Z., Liu, X. F., & Xie, J. X. 2012. Effect of Γ2 Phase Evolution on Mechanical Properties of Continuous Columnar-Grained Cu–Al–Ni Alloy. *Materials Science and Engineering: A*, 532, 536-542.
- [14] Tatar, C., & Kazanc, S. 2012. Investigation of the Effect of Pressure on Thermodynamic Properties and Thermoelastic Phase Transformation of Cualni Alloys: A Molecular Dynamics Study. *Current Applied Physics*, 12(1), 98-104.
- [15] Husain S W. 1984. PhD Thesis University of Connecticut
- [16] Sugimoto K et al .1982. J. Physique Coll. 43 C4 761
- [17] Sampath, V. 2005. Studies on the Effect of Grain Refinement and Thermal Processing on Shape Memory Characteristics of Cu–Al–Ni Alloys. *Smart Materials And Structures*, 14 (5), S253.
- [18] Sari, U. (2010). Influences of 2.5 wt% Mn Addition on the Microstructure and Mechanical Properties of Cu-Al-Ni Shape Memory Alloys. *International Journal of Minerals, Metallurgy, and Materials*, 17 (2), 192-198.
- [19] Dunne D.P. and .Kennon N.F. Metals Forum, 1981, 4, p.176.
- [20] Recarte, V., et al. 1999. Dependence of the Martensitic Transformation Characteristics on Concentration in Cu–Al–Ni Shape Memory Alloys. *Materials Science and Engineering: A*, 273, 380-384.
- [21] Elif Tarhan, M.Sc. Thesis, Middle East Technical University, 1996.
- [22] Morawiec, H., & Gigla, M. 1995. Precipitation and Shape Recovery in CuAlNi+ TiB Alloy. *Le Journal de Physique IV*, 5 (C2), C2-193.
- [23] Wei, Z. G., Peng, H. Y., Zou, W. H., & Yang, D. Z. 1997. Aging Effects in a Cu-12Al-5Ni-2Mn-1Ti Shape Memory Alloy. *Metallurgical and Materials Transactions A*, 28(4), 955-967.
- [24] Marukawa K., Tsuchiya K. and Arai Y., ICOMAT'95, 1995, pp. C8-841.
- [25] Suresh, N., & Ramamurty, U. 2008. Aging Response and Its Effect on the Functional Properties of Cu–Al–Ni Shape Memory Alloys. *Journal of Alloys* and Compounds, 449(1), 113-118.
- [26] Jan Van Humbeeck, Shape Memory Alloys. CRC Press, 2009, p. 20.

- [27] Balo, Ş. N., & Sel, N. 2012. Effects of Thermal Aging on Transformation Temperatures and Some Physical Parameters of Cu–13.5 wt.% Al–4wt.% Ni shape memory alloy. *Thermochimica Acta*.
- [28] Saud, S. N., Hamzah, E., Abubakar, T., & Farahany, S. 2013. Structure-Property Relationship of Cu-Al-Ni-Fe Shape Memory Alloys in Different Quenching Media. *Journal of Materials Engineering and Performance*, 1-7.