



MARTENSITE CHARACTERISTIC TEMPERATURE (M_f) and MECHANICAL PROPERTIES of SUBZERO QUENCHED and AGED TC21 α/β TITANIUM ALLOY

By

Rania Mohamed Sayed El-Shorbagy

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING

MARTENSITE CHARACTERISTIC TEMPERATURE (M_f) and MECHANICAL PROPERTIES of SUBZERO QUENCHED and AGED TC21 α/β TITANIUM ALLOY

By Rania Mohamed Sayed El-Shorbagy

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING

Under the Supervision of

Prof. Dr. AbdelHamid A. Hussein	Prof. Dr. El-Sayed M. El-Banna
Professor of Metallurgy	Professor of Metallurgy
Metallurgical Engineering Department	Metallurgical Engineering Department
Faculty of Engineering, Cairo University	Faculty of Engineering, Cairo University
Prof. Dr. El-Zahraa M. El-Baradie	Prof. Dr. Mohamed A. Waly
Professor of Metallurgy	Professor of Metallurgy
Central Metallurgical Research and	Central Metallurgical Research and
Development Institute	Development Institute

FACULTY OF ENGINEERING, CAIRO UNIVERSITY GIZA, EGYPT 2020

MARTENSITE CHARACTERISTIC TEMPERATURE (M_f) and MECHANICAL PROPERTIES of SUBZERO QUENCHED and AGED TC21 α/β TITANIUM ALLOY

By Rania Mohamed Sayed El-Shorbagy

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING

Approved by the Examining Committee

Prof. Dr. AbdelHamid Ahmed Hussein Thesis Main Advisor

Prof. Dr. El-Sayed Mahmoud El-Banna Advisor

Prof. Dr. El-Zahraa M. El-Baradie Advisor

Central Metallurgical Research and Development Institute (CMRDI)

Prof. Dr. Mohamed A. Waly Advisor

Central Metallurgical Research and Development Institute (CMRDI)

Prof. Dr. Mohamed Mamdouh Ibrahim Internal Examiner

Prof. Dr. Adel Abdel Moneim Nofal External Examiner

Central Metallurgical Research and Development Institute (CMRDI)

FACULTY OF ENGINEERING, CAIRO UNIVERSITY GIZA, EGYPT 2020 **Engineer's Name:** Rania Mohamed Sayed El-Shorbagy

Date of Birth: 27/2/1987 **Nationality:** Egyptian

E-mail: Eng.raniamohamed10@gmail.com

Phone: 01004568283

Address: 32 Om El-qura St. Warraq

Registration Date: 1/10/2015 **Awarding Date:**/2020

Degree: Doctor of Philosophy **Department:** Metallurgical Engineering

Supervisors:

Prof. Dr. AbdelHamid Ahmed Hussein Prof. Dr. El-Sayed Mahmoud El-Banna Prof. Dr. El-Zahraa M. El-Baradie

Central Metallurgical Research and Development Institute (CMRDI)

Prof. Dr. Mohamed A. Waly

Central Metallurgical Research and Development Institute (CMRDI)

Examiners:

Porf. Dr. AbdelHamid A. Hussein (Thesis main advisor)

Porf. Dr. El-Sayed M. El-Banna (Advisor) Prof. Dr. El-Zahraa M. El-Baradie (Advisor)

Central Metallurgical Research and Development Institute (CMRDI)

Prof. Dr. Mohamed A. Waly (Advisor)

Central Metallurgical Research and Development Institute (CMDIR)
Prof. Dr. Mohamed Mamdouh Ibrahim (Internal examiner)
Prof. Dr. Adel Abdel Moneim Nofal (External examiner)
Central Metallurgical Research and Development Institute (CMRDI)

Title of Thesis:

Martensite characteristic temperature (M_f) and mechanical properties of subzero quenched and aged TC21 α/β titanium alloy

Key Words:

TC21 α/β titanium alloy microstructure; Subzero hardening; Titanium martensite characteristic temperature; Aging; Mechanical properties.

Summary:

Titanium alloys are known to experience martensite transformation, their martensite and its transformations upon subsequent heat treatment proved to be an important tool to obtain controllable properties. The martensite characteristic temperature (M_s) has received some attention as regards its dependence on composition. On the other hand, no similar attention was given to the dependence of the other important martensitic characteristic temperature (M_f) on composition. In view of the foregoing, this work was thus planned to fulfill this lacking information via subzero hardening treatments of TC21 α/β alloy. Additionally, the hardening effect of those subzero hardening treatments was studied. Significant findings were reached which are expected to help reaching useful property levels such as strength, wear resistance and damage tolerance. Correlation between strength and Vickers hardness values were obtained by means of least squares mathematical analysis. Simple empirical equations were suggested to evaluate the strength using bulk hardness. The present largest tensile strength values approach 1200 MPa in the quenched condition and 1700 MPa in the aged condition. This prominent hardening of the subzero quenched and post aged microstructures can lead to useful overall properties of this TC21 α/β titanium alloy.



Disclaimer

I hereby declare that this thesis is my own original work and that no part of it has been submitted for a degree qualification at any other university or institute.

I further declare that I have appropriately acknowledged all sources used and have cited them in the references section.

Name: Rania	Mohamed 3	Sayed El-Shorb	oagy	Date:	/	/
Signature:						

Dedication

I dedicate this thesis to my family.

Acknowledgments

All gratitude is due to Allah who guided me and showed me the right path, without his help my efforts would have gone astray.

My greatest thanks to Prof. Dr. AbdelHamid Ahmed Hussein, Professor of metallurgy, Faculty of Engineering, Cairo University, for his guidance and supervision. He has been very helpful in improving dissertation. I am grateful to his for sharing his time and expertise. His comments and views were very insightful and helpful. It would have not been possible for me to bring out this thesis without his help and constant encouragement.

I would like to thank deeply prof. Dr. El-Zahraa Mohamed Yehia El-Baradie, Professor of metallurgy, Central Metallurgical Research and Development Institute, for her guidance and supervising this thesis.

My special thanks to prof. Dr. El-Sayed Mahmoud El-Banna, Professor of metallurgy, Faculty of Engineering, Cairo University, for his support in the completion of the thesis.

My deep thanks to Prof. Dr. Mohamed Abdel Wahab Waly, Professor of metallurgy, Central Metallurgical Research and Development Institute, for his help in the completion of the thesis.

Thanks are to all of my friends, especially Lamiaa Zaki Mohamed and Hayam Abokhasha for their help and support.

Finally, a very special thanks to my parents and my husband for their support, encouragement and trust in me throughout my life.

Table of Contents

DISCLAIMER	I
DEDICATION	II
ACKNOWLEDGMENTS	III
TABLE OF CONTENTS	IV
LIST OF TABLES	VII
LIST OF FIGURES	VIII
ABSTRACT	XIII
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: LITERATURE REVIEW	3
2.1 Metallurgy of Ti and Ti-alloys	3
2.2 Alloying elements of Ti	4
2.2.1 α stabilizers	4
2.2.2 β stabilizers.	4
2.2.3 Neutral elements.	5
2.3 Classification of Ti alloys.	5
2.3.1 Commercially pure titanium and α alloys	6
2.3.2 Near α alloys.	7
$2.3.3 \ \alpha/\beta \ alloys$	7
2.3.4 Metastable β alloys.	8
2.3.5 Stable β alloys.	9
2.4 Alloy design.	9
2.5 Transformation mechanism in Ti alloys	9
2.5.1 Nucleation and diffusional growth.	10
2.5.2 Martensite transformation.	11
2.6 Phases in titanium alloys.	13
2.6.1 α phase	13
2.6.1.1 Primary α phase (α_p)	13
2.6.1.2 Secondary α phase (α_s)	13
2.6.1.3 α ₂ phase (Ti ₃ Al)	13

2.6.1.4 Hexagonal martensite phase (α')
2.6.1.5 Orthorhombic martensite phase (α")
2.6.2 β phases
2.6.2.1 Equilibrium β phase
2.6.2.2 β flecks
2.6.2.3 Metastable β phase
2.7 Heat treatment of Ti alloys
2.7.1 Age hardening
2.7.2 annealing.
2.8 Microstructure and processing of α/β titanium alloy
2.8.1 Fully lamellar microstructure
2.8.2 bi-modal microstructure
2.8.3 Fully equiaxed microstructure.
2.9 Microstructural effect on the mechanical properties of α/β alloy
2.10 Effect of heat treatment process on mechanical properties of TC21 alloy
2.11 Characteristics and applications of Ti alloys.
2.11.1 Ti alloys for biomedical applications
2.11.2 Ti alloys for aerospace industry
2.11.3 Ti alloys for Automotive Applications
CHAPTER 3: EXPERIMENTAL WORK
3.1. Material
3.2. Heat treatment
3.3 Microstructure examination.
3.4 Mechanical testing.
3.4.1 Macro and microhardness test.
CHAPTER 4: RESULTS AND DISCUSSION
4.1 Microstructure evolution.
4.1.1 As-received condition.
4.1.2 As quenched state
4.1.2.1 Water quenching to room temperature
4.1.2.2 Quenching to subzero temperatures
4 1 2 2 1 900 °C quench temperature

4.1.2.2.2 940 °C quench temperature	39
4.1.2.2.3 980 °C quench temperature	41
4. 1. 3 Estimation of M _f martensite characteristic temperature	43
4. 1. 4 Aged condition	45
4.1.4.1 Effect of aging after quenching to room temperature on microstructure and phase transformation.	45
4.1.4.2 Effect of aging after subzero quenching on microstructure and phase transformation after solid solution from 900 °C	48
phase transformation after solid solution from 940 °C	50
phase transformation after solid solution from 980 °C	52
4.2 Mechanical properties	54
4.2.1 Hardness	54
4.2.1.1 As quenched condition	54
4.2.1.2 Aged condition	56
4.2.2 Microhardness analysis	59
4.3 Correlation of strength and hardness	60
Chapter 5: CONCLUSIONS	65
REFERENCES	67

List of Tables

Table 2.1: Effect of solution treating temperature on tensile properties of TC21 alloy	16
Table 3.1: Chemical composition of as-received TC21Ti-alloy (wt. %)	28

List of Figures

Fig. 2.1. a) Classification of the alloying elements of titanium according to their influence on the β -transus temperature, T_{β} . b) Lattice correspondence between the	
hcp α and bcc β structures. The lattice parameters correspond to the values of pure titanium at RT and 900 °C for α and β , respectively	3
Fig. 2. 2. Influence of alloying elements on phase diagrams of Titanium alloys	5
Fig.2.3. Classification of titanium alloys in the β isomorphous phase diagram (pseudo-binary section)	6
Fig.2.4. Variations of physical, chemical, mechanical and technological properties for the different groups of titanium alloys and their association with alloying and processing methods.	9
Fig.2.5. The effect of the cooling rate on the constitution of an α/β alloy	10
Fig.2.6. Schematic illustration of the formation of a Widmanstätten structure by cooling slowly from above the β transus	11
Fig.2.7. Schematic processing steps for the lamellar microstructure	17
Fig.2.8. Schematic representation of α/β titanium alloys	18
Fig.2.9. Schematic processing steps for the bimodal microstructure	19
Fig.2.10. a) Processing route and b) fully equiaxed microstructure of α/β alloys slowly cooled in step III	20
Fig.2.11. Processing route for fully equiaxed microstructures of α/β alloys recrystallized at low temperatures.	21
Figure 2.12. Curves of the mechanical properties vs. solution temperature for TC21 titanium alloy (a) YS, (b) UTS, (c) Z, (d) A and (e) K _{IC}	22
Figure 2.13: Variation of microhardness of TC21 titanium alloy with solution treatment temperature	23
Figure 2.14. Effect of different cooling rates and aging on tensile strength of TC21 alloy	24
Fig. 2.15. Titanium dental tools, surgical screws, and implants	25
Fig.2.16. Titanium plug implanted into a human cheek bone into which is screwed an artificial tooth. The rough surface promotes bone adhesion to the titanium screw	25

Fig. 2.17. (a) Material selection for airframes and gas turbine engines of novel commercial aircrafts (percentage of structural weight). (b) Evolution of the demand of titanium in the last decade for the largest producers of commercial aircrafts.	26
Fig. 2.18. Effect of automobile weight on fuel consumption	27
Fig. 2.19. Possible applications for titanium in a passenger automobile	27
Fig. 3.1: Vertical tube furnace for solid solution.	29
Fig. 3.2. Experimental procedure for the heat treatment	29
Fig. 3.3: Optical microscope/model OLYMPUS BX41M-LED.	30
Fig. 3.4: SEM/model QUANTA FEG 250.	31
Fig. 3.5: XRD/ ARL X'TRA	31
Fig. 3.6: (a)Vickers hardness tester/ZWICK/Roell ZHU250 and (b) Microhardness test/ model HMV-SHIMADZU.	32
Fig. 4.1. Optical micrograph of the as received TC21 alloy	33
Fig. 4.2. SEM micrograph of as received TC21 alloy.	33
Fig. 4.3. XRD pattern of the as-received TC21 alloy	34
Fig. 4.4. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 900°C to room temperature	35
Fig. 4.5. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 940°C to room temperature	35
Fig. 4.6. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 980°C to room temperature.	35
Fig. 4.7. XRD patterns of the solution treated samples quenched to room temperature.	37
Fig. 4.8. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 900°C to 0 °C.	38
Fig. 4.9. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 900°C to -20 °C.	38
Fig. 4.10. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 900°C to -40 °C.	38

Fig. 4.11. XRD patterns of as quenched samples from 900 °C to subzero temperatures (0, -20 and -40 °C)	39
Fig. 4.12. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 940°C to 0 °C	40
Fig. 4.13. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 940°C to -20 °C.	40
Fig. 4.14. Optical micrograph of TC21 alloy quenched from 940°C to -40 °C	40
Fig. 4.15. XRD patterns of as quenched samples from 940 °C to subzero temperatures (0, -20 and -40 °C)	41
Fig.4.16. Optical micrograph of TC21 alloy quenched from 980°C to 0 °C	42
Fig.4.17. Optical micrograph of TC21 alloy quenched from 980°C to -20 °C	42
Fig.4.18. (a) Optical and (b) SEM micrographs of TC21 alloy quenched from 980°C to -40 °C.	42
Fig. 4.19. XRD patterns of as quenched samples from 980 °C to subzero temperatures (0, -20 and -40 °C)	43
Fig. 4. 20. (a) Hypothetical phase diagram illustrating the location of quench temperatures and composition of the corresponding β phase, and (b) Variation of M_f temperature with [Mo]eq. as calculated from the composition of the corresponding β phase at each quench temperature, where :point (1) Based on the original composition (quenched $Tq > T\beta$), point (2) β composition based on EDX analysis of martensite, and point (3) β composition, extrapolated	44
Fig. 4.21. Micrographs of aged sample prequenched from 900 °C to room temperature: a) Optical image and b) SEM image	46
Fig. 4.22. Micrographs of aged sample prequenched from 940 °C to room temperature: a) Optical image and b) SEM image	46
Fig. 4.23. Micrographs of aged sample prequenched from 980 °C to room temperature: a) Optical image and b) SEM image	47
Fig. 4.24. XRD patterns of the aged samples prequenched to room temperature	47
Fig. 4.25. Micrographs of aged sample prequenched from 900 °C to 0 °C: a) Optical image and b) SEM image	48
Fig. 4.26. Micrographs of aged sample prequenched from 900 °C to -20 °C: a) Optical image and b) SEM image.	49
Fig. 4.27. Micrographs of aged sample prequenched from 900 °C to -40 °C: a) Optical image and b) SEM image	49

Fig. 4.28. XRD patterns of the aged samples prequenched from 900 °C to subzero temperatures (0, -20 and -40 °C).	50
Fig. 4.29. Micrographs of aged sample prequenched from 940 °C to 0 °C: a) Optical image and b) SEM image	51
Fig. 4.30. Micrographs of aged sample prequenched from 940 °C to -20 °C: a) Optical image and b) SEM image	51
Fig. 4.31. Micrographs of aged sample prequenched from 940 °C to -40 °C: a) Optical image and b) SEM image	51
Fig. 4.32. XRD patterns of the aged samples prequenched from 940 $^{\circ}$ C to subzero temperatures (0, -20 and -40 $^{\circ}$ C).	52
Fig. 4.33. Micrographs of aged sample prequenched from 980 °C to 0 °C: a) Optical image and b) SEM image	53
Fig. 4.34. Micrographs of aged sample prequenched from 980 °C to -20 °C: a) Optical image and b) SEM image	53
Fig. 4.35. Micrographs of aged sample prequenched from 980 °C to -40 °C: a) Optical image and b) SEM image	53
Fig. 4.36. XRD patterns of the aged samples prequenched from 980 $^{\circ}$ C to subzero temperatures (0, -20 and -40 $^{\circ}$ C).	54
Fig. 4.37. Average hardness values of solid solution heat treated conditions	56
Fig. 4.38. Average hardness values of aged conditions	57
Fig. 4.39. Comparison between the hardness of solid solution and aged condition	58
Fig. 4. 40. TEM micrographs showing primary α , secondary α and martensite in quenched and aged TC21 samples.	58
Fig. 4.41. Photomicrographs of microhardness indentations of: a) Sample quenched from 940 $^{\circ}$ C to 0 $^{\circ}$ C, and b) Aged condition	59
Fig. 4.42. Photomicrographs of microhardness indentations of: a) Sample quenched from 940 °C to -20 °C, and b) Aged condition	60
Fig. 4.43. Photomicrographs of microhardness indentations of: a) Sample quenched from 980 °C to 0 °C, and b) Aged condition	60
Fig. 4.44. Correlation of hardness and ultimate tensile strength for different titanium alloys	62
Fig. 4.45. Correlation between hardness and yield strength for titanium alloys	62