

**STUDIES ON CERTAIN ASPECTS OF
Ti, AND Ti, Co, Ni AND Cu ALLOYS
AS
POTENTIAL DENTAL MATERIALS**

BY

RAMESH KUMAR MEHTA

M.Tech., PGDMS (I.I.T., DELHI)

*Thesis submitted
in fulfilment of the requirements
for the award of the degree of
DOCTOR OF PHILOSOPHY*

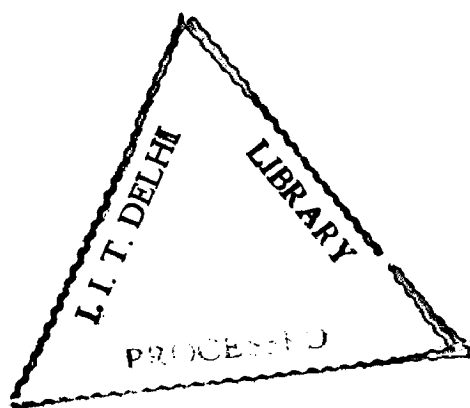
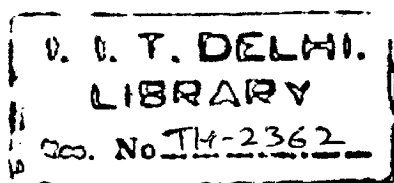


to the

**INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NEW DELHI - 110 016, INDIA**

MARCH, 1996

TH
669-1:616.314
MEN-S



DEDICATED

to

My Wife Neelu

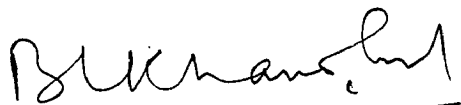
&

Sons Ankush & Akshay

CERTIFICATE

This is to certify that the thesis entitled, "**Studies on Certain Aspects of Ti, and Ti, Co, Ni and Cu Alloys as Potential Dental Materials**", being submitted by **Mr. Ramesh Kumar Mehta**, to the Indian Institute of Technology, Delhi, for the award of degree of '*Doctor of Philosophy*' in Chemistry, is a record of bonafide research work carried out by him. Mr. Mehta has worked under our guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to our knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.



SUPERVISOR

PROFESSOR B.L. KHANDELWAL
Department of Chemistry
Indian Institute of Technology, Delhi
New Delhi - 110 016
INDIA.



CO-SUPERVISOR

DR. T. RAVINDRANATH
Head, Department of Dental Res.
I.N.M.A.S, D.R.D.O.
Delhi - 110 054
INDIA.

ACKNOWLEDGEMENT

I extend my deep sense of gratitude to my supervisor, **Prof. B.L. Khandelwal** for his advice, untiring efforts, constant inspiration and constructive criticism during the course of this investigation.

I am also thankful to my co-supervisor, **Dr. T. Ravindranath** who has supported the study and advised and helped me in conducting the biocompatibility studies.

I am extremely thankful to **Shri Narender Singh**, Scientist-G, Director, Technical Coordination and **Maj. Gen. R. Swaminathan**, Chief of Resources who have given permission to conduct the study and motivated me from time to time. Thanks are also especially extended to **Dr. I.D. Gaba** for his all time moral support during the course of this study.

I also extend my sincere thanks to Prof. N.K. Jha, Head, Department of Chemistry, Indian Institute of Technology, Delhi, and Prof. V.K. Jain, Director, INMAS, DRDO, Delhi for providing me the necessary facilities.

My sincere thanks are due to Dr. R.K. Nigam, Mr. H.L. Chhatwal, Mr. R.K. Sharma, Mr. K.K. Vadera, Mr. S.V. Athavale, Mrs. N. Rukmani Desikan, Mr. S.R. Gupta, Dr. R.P. Mall and Mr. Ramesh Kumar for their help in extending the lab facilities. Thanks are also especially extended to my colleagues Mr. V. Gulwani, Jt. Director, Mr. K.M. Varma and Mr. Dinesh Kumar of DRDO Hqr. for their moral support.

I would like to express my deep regards and thanks to my grand mother-in-law, parents, parents-in-law and mataji for boosting my morale throughout the course of this work.

I would especially like to thank my wife Mrs. Neelu and my sons Master Ankush and Master Akshay for their moral support and untiring patience with me throughout this study.

I am thankful to lab staff, Mr. Q.U. Khan, Mr. Gautam Kar and Mr. H.K. Varma of INMAS, and Mr. Narayan Singh and Mr. Ved Prakash of I.I.T. for their help in laboratory work.


RAMESH KUMAR MEHTA

ABSTRACT

The work presented in the thesis entitled, "***Studies on certain aspects of Ti, and Ti, Co, Ni and Cu alloys as potential dental materials***" consists of investigations of their chemical composition, invitro electrochemical behaviour, and probable phases and casting defects (viz. surface topographical changes) produced on casting. The investigations related to the effects of disinfectants on selected alloys, surface science aspects of titanium and the influences of intentionally generated different surface topographical characteristics of titanium on its osseointegration have also been carried out. The main aim of the present study has been to understand the behavioural aspects of titanium and some alloys, and to study their suitability for clinical applications as potential dental materials.

The chemical composition of different batches of newly developed Ti, its alloys, viz. Ti-10Co and Ti-20Co, and Ni-Cr, Co-Cr-Mo, Co-Cr-Mo-Si and Cu-Ni-Al alloys has been determined by H, CS and ON analysers, and atomic absorption spectroscopic technique.

The invitro electrochemical behaviour has been studied by electrochemical measurement systems in saline and saliva media under the aerated environment to understand the overall electrochemical behaviour, to investigate the effects of chemical composition on their corrosion behaviour, and to quantify the corrosion rate of these potential materials for dental applications. The mechanism of corrosion of these materials under the media of

study has been proposed. The study has been conducted adopting open circuit potential and polarisation resistance techniques to evaluate their nobility, stability and passivity, and anodic and cathodic polarisation techniques to evaluate anodic and cathodic Tafel constants, and also to determine the corrosion current densities and corrosion rates for comparison of these materials in saline and saliva media. The potentiodynamic polarisation, cyclic polarisation and corrosion behaviour diagram techniques have been further adopted to understand and compare their passivation tendency, relative stability of passive film, active to passive transition, pitting and crevicing tendency, and overall electrochemical behaviour of these materials. It is inferred from the data that all the materials show rise in potential in noble (positive) direction and stabilization within an hour. In saline medium the order of corrosion rate is Co-Cr-Mo-Si < Co-Cr-Mo < Ti-10Co < Ni-Cr(BC) < Cu-Ni-Al < Ti-20Co < Ni-Cr(LC) < Ti, and in saliva medium the order is Ni-Cr(BC) < Co-Cr-Mo $\approx$ Co-Cr-Mo-Si < Ni-Cr(LC) < Ti-10Co < Ti < Ti-20Co < Cu-Ni-Al [BC means bulk cast and LC means lab cast]. The very low calculated values of corrosion current densities and corrosion rates are indicative of their higher corrosion resistance. The Ni-Cr and Cu-Ni-Al alloys have shown pitting tendency and poor nature of passive film. The sample surfaces have also been examined by scanning electron microscope (SEM) before and after polarisation to reveal the modes of corrosion. The scanning electron micrographs suggest that there is general corrosion of all materials.

The materials have been investigated by XRD technique for probable phases present in them. The diffractograms and data suggest that Ti has h.c.p. α phase structure, and Ti-Co alloys have b.c.c. β -Ti and f.c.c. Ti_2Co like phases, and Ni-Cr indicates cubic Ni and f.c.c. γ' - Ni_3Al like phase structures. In case of Cu-Ni-Al the study indicates the presence of f.c.c. α -Cu, h.c.p. β^1 - Cu_3Al_2 and cubic γ - Cu_9Al_4 probable phases, where as in Co alloys the phases are h.c.p. α -Co and f.c.c. β -Co like. The addition of Si gives indication of h.c.p. CoMoSi as probable third phase.

The casting defects and pits (viz. surface topographical changes) generated on bulk and lab casting have been investigated using SEM by recording their secondary electron images. The SEM scans of Ti-Co alloys show dendrite regions with distributed shrinkage and porosity, and those of Co-Cr-Mo alloys show arrays of dendrites and widely distributed defects with large and circular pits and reduced shrinkage. The Co-Cr-Mo-Si alloy has shown reduced casting defects. The Ni-Cr alloy shows small but scattered pits with reduced casting defects, viz. microporosity. The observations in general correlate with other studies.

The post-reaction effects of disinfectants on selected alloys have been studied by optical microscopic (OM), profilometric scanning (PS) and SEM techniques. The concentrated solutions (10% by volume and more) of NaOCl-10% produced marked small pits and enlarged old pits with no discernible grain structure. The phenol based disinfectant (cidex-7) is found to be safe even at higher concentrations. Overall, these disinfectants produce least

pitting corrosion on Ni-Cr alloy, and minor adverse effects on Co-Cr-Mo and Co-Cr-Mo-Si alloy surfaces.

The influences of various surface preparative procedures on potential implant material, e.g. Ti, have been studied under controlled etching parameters to evaluate percent weight loss (etching rate) by percent weight loss measurements and surface topography by OM, PS and SEM techniques. The improved uniform surface roughness, i.e. microstructure has been observed on titanium samples after reactions with HCl-H₂SO₄ acid mixtures, when compared with conventionally prepared samples.

The biocompatibility studies by radiographic, OM, PS and SEM techniques reveal significantly higher percent level of osseointegration in chemically reacted screw type Ti implant samples.

CONTENTS

CHAPTER-I GENERAL INTRODUCTION

1.1	INTRODUCTION	1
1.2	METALS AND ALLOYS IN SURGERY / DENTISTRY	1
1.3	CURRENTLY USED METALS AND ALLOYS IN SURGERY / DENTISTRY	3
1.3.1.	<i>Precious Metals Based Alloys</i>	4
1.3.2.	<i>Austenitic Stainless Steel Alloys</i>	4
1.3.3.	<i>Nickel-Chromium Based Alloys</i>	5
1.3.4.	<i>Cobalt-Chromium Based Alloys</i>	7
1.3.5.	<i>Copper Based Alloys</i>	8
1.3.6.	<i>Titanium and Its Alloys</i>	10
1.4	GENERAL REQUIREMENTS FOR DENTAL MATERIALS	12
1.5	FACTORS AFFECTING DENTAL MATERIALS	13
1.5.1.	<i>Biological Factors</i>	13
1.5.2.	<i>Mechanical and Chemical Factors</i>	15
1.6	PRESENT STUDY : OBJECTIVES AND SCOPE	18
	TABLES	21

CHAPTER-II MATERIALS AND METHODS

2.1	ELEMENTAL ANALYSES	29
2.2	INVITRO ELECTROCHEMICAL BEHAVIOUR STUDIES	31
2.3	X-RAY DIFFRACTION (XRD) STUDIES	37
2.4	SCANNING ELECTRON MICROSCOPIC (SEM) STUDIES	38
2.5	EFFECTS OF DISINFECTANTS	38
2.6	SURFACE SCIENCE ASPECTS	40

CHAPTER-III RESULTS AND DISCUSSION

3.1	ELEMENTAL ANALYSES	44
3.2	INVITRO ELECTROCHEMICAL BEHAVIOUR STUDIES	45
3.2.1.	<i>Open Circuit Potential (OCP) Study</i>	47
3.2.2.	<i>Anodic and Cathodic Polarisation Studies</i>	48
3.2.3.	<i>Polarisation Resistance Study</i>	50
3.2.4.	<i>Potentiodynamic Polarisation Study</i>	52
3.2.5.	<i>Cyclic Polarisation Study</i>	53
3.2.6.	<i>Corrosion Behaviour Diagram (CBD) Study</i>	57
3.2.7.	<i>Scanning Electron Microscopic (SEM) Study</i>	60
3.2.8.	<i>Conclusions</i>	62
	TABLES	64
	FIGURES	
3.3	X-RAY DIFFRACTION (XRD) STUDIES	71
	Conclusions	87
	TABLES	89
	FIGURES	
3.4	SCANNING ELECTRON MICROSCOPIC (SEM) STUDIES	99
	Conclusions	102
	FIGURES	
3.5	EFFECTS OF DISINFECTANTS	104
3.5.1.	<i>Optical Microscopic (OM) Study</i>	105
3.5.2.	<i>Profilometric Scanning (PS) Study</i>	106
3.5.3.	<i>Scanning Electron Microscopic (SEM) Study</i>	108
3.5.4.	<i>Conclusions</i>	110
	TABLES	111
	FIGURES	
3.6	SURFACE SCIENCE ASPECTS	113
3.6.1.	<i>Percent Weight Loss Measurements</i>	115
3.6.2.	<i>Optical Microscopic (OM) Study</i>	116
3.6.3.	<i>Profilometric Scanning (PS) Study</i>	118
3.6.4.	<i>Scanning Electron Microscopic (SEM) Study</i>	120
3.6.5.	<i>Conclusions</i>	122

TABLES	124
FIGURES	

CHAPTER-IV BIOCOMPATIBILITY STUDIES

4.1	INTRODUCTION	126
4.2	MATERIALS AND METHODS	129
4.3	RESULTS AND DISCUSSION	130
	<i>4.3.1. Radiographic Study</i>	<i>130</i>
	<i>4.3.2. Optical Microscopic (OM) Study</i>	<i>131</i>
	<i>4.3.3. Scanning Electron Microscopic (SEM) Study</i>	<i>133</i>
4.4	CONCLUSIONS	134

FIGURES

CHAPTER-V SUMMARY AND FURTHER SCOPE OF THE WORK

5.1	SUMMARY OF THE WORK	136
5.2	FURTHER SCOPE OF THE WORK	144

FIGURE

REFERENCES	146
-------------------	------------