## PHASE TRANSFORMATIONS

# IN THE TITANIUM-NIOBIUM BINARY ALLOY SYSTEM

by

David L. Moffat

# A thesis submitted in fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

(Materials Science)

at the

UNIVERSITY OF WISCONSIN - MADISON

1985

The Forder Bally Bay - - -

<u>`</u>\_\_

a na ann an an ann an Arthreach

#### ABSTRACT

#### PHASE TRANSFORMATIONS

#### IN THE TITANIUM-NIOBIUM BINARY ALLOY SYSTEM

#### David L. Moffat

Under the supervision of Professor David C. Larbalestier

A fundamental study of the phase transformations which occur in the Ti-Nb binary alloy system has been completed. Eight alloys in the range 20 to 70 at% Nb were investigated using transmission electron microscopy, light metallography and x-ray diffraction. Measurements of electrical resistivity and Vicker's microhardness also were Emphasis was placed on the minimization of interstitial performed. contamination in all steps of alloy fabrication and specimen preparation. In order to eliminate the effects of prior cold-working, alloys studied were recrystallized 1000C. the at Phase transformations were studied in alloys which had been quenched to room temperature after recrystallization, quenched to room temperature and then isothermally aged, and in those which had been isothermally aged without a prior room temperature quench. It was found that the microstructures of the quenched 20 and 25% Nb alloys were extremely sensitive to quench rate -- with a fast quench producing martensite, a slow quench, the omega phase. The microstructures of the higher

niobium content alloys were much less sensitive to quench rate. The microstructures of the isothermally aged 20 and 25% Nb alloys were found to be sensitive to prior thermal history. Alloys quenched to room temperature and then aged at 400C contained large omega precipitates, while those aged without an intermediate room temperature quench contained alpha precipitates. Isothermal omega phase precipitation was found in quenched 20 and 25% Nb specimens aged at 300, 350 and 400C. The 35% Nb alloys aged between 300 and 500C contained precipitates which could not be identified using electron diffraction, but were determined to be nuclei of the alpha phase. Aging at 450, 500 and 600C produced alpha precipitates in the 20 to 40% Nb alloys. The beta transus in this system could not be determined unambiguously. A phase diagram was calculated which fit the experimental data, but also predicted a small, but stable, beta phase miscibility gap.

## Approved:

#### David C. Larbalestier

#### ACKNOWLEDGEMENTS

There are many people at the University of Wisconsin whom I wish to thank for their help and support. First among these is David Larbalestier, under whose guidance years of slow and deliberate study have finally lead to fruition. I wish to thank John Perepezko for many helpful and interesting discussions — he made time for me where others would not have. The several conversations with Anne West, before her departure from the UW, are greatly appreciated, as are the advice of and discussions with those in the Superconducting Materials Research Group. Without the diligent, and often extraordinary, efforts of Richard Casper in maintaining the facilities of the Materials Science Program, the electron microscopy and x-ray diffraction experiments of my work would have been severely curtailed. The friendship of several other students and faculty in the Materials Science and Metallurgy departments have made the years more enjoyable.

Over the years I have had the opportunity to work with several undergraduates to whom was relegated much of the less glamorous support work. I would like to thank Beth Maynard, Beran Tari and John Goddard for all their efforts on my behalf. (I am particularly indebted to John, for, without his help, the final production of this thesis would have been impossible.) These three were intelligent and diligent workers who could be counted on to do more than was asked, often with impossible time limitations. They were also good friends.

I would also like to thank Ann, my parents and hers for their years of patience, understanding and support. Upon acceptance of this thesis, I may finally graduate into the "real world."

# TABLE OF CONTENTS

.

.

ABSTRA	ст	••	•	•	•	•	•	•	•		٩	٠	•	•	•		•	•	٠	•	•	¥	•	٠	•		•	1	
ACKNOL	WEDGEMI	INTS	•	٠	٠	•	•	•	•	•	•	•	•	•	٠	•	•	•	•		•	•	•	٠	•	•	ź	Lii	
LIST O	f Tabli	es.	•	•	•	•	•	•	•	•	•	•	•	•	*	•	•	•		•	•	•	•			*	*	ix	
LIST O	F FIGUI	RES	•	٠	٠	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	<b>#</b> 1	•	xi	
CHAPTE:	R ONE ·	- Int	ro	du	.ct	io	n	•	•	•	•	•	•	•	•	•	•	•	,	•	•	•	•	•	•	•	•	1	
	XIOMEIII		~1 0	,	•	•	•	•	•	•	•	•		•		•	•	•		•	•	•		•	•	•	Ĩ	2	
CHAPTE	R TWO	- Spe	≥ci	me	n	Pr	ep	ar	at	, ic	n	ar	ıd	Ез	cpe	ri	me	nt	al	. 1	lec	hr	nig	ue	8	•	•	8	
2.1	Introd	iucti	Lon	L	•	•	•		•	•	. •	•	•		•	•	•	•		•	•	+	•	•	•	•	•	9	
2.2	Alloy	Fab	cic	at	io	n	•	•	•	•	• ,	•	•	•	•	•	•	•	•	•	•	÷	•	•	•	•	•	10	
2.3	Heat !	Freat	me	nt	Т	ec	hn	ig	lne	1	•	•	•	•	•	•	•	•		•		•	•	•		•		19	
	2.3.1	Que	enc	h1	ng		•	•	•	•		•	•	•		•	•		•	•	•		•	+		•	•	20	
2.4	Resist	ivit	y	Me	as	ur	eπ	ien	its	ł	•	•	*			•	•	•					•	•		•	•	24	
2.5	Light	Meta	a11	.og	ra	ph	У	•	•	•	•		•	•	•	•	•	•					•		٠	•	•	24	
2.6	Transı	nissi	Lon	E	le	ct	ro	n	Mi	cı	:08	ec	<b>P</b> Z	,	*	•	•	•	•				•	•	•	•	•	27	
2.7	X-ray	Difi	Era	ct	io	n	•	•	•	•	•	•	•	•	•	•	•	•			•	•		•	+	•	•	28	
2.8	Summat	cy.																										31	

v

CHAPTE	R THREE	- Metastabl	Le Equil	ibria	<b>.</b>	•	•	• •	٠		•	•	• •	• •		٠	33
3.1	Introd	uction			• •	•	•	• •	•	•	•		•	• •	*		34
3.2	Marten	sitic Phases			•••	•	*	• •	•	•	•	•		•		•	36
	3.2.1	Crystal St	ructures	and	Ori	ent	at:	ion	Re	la	ti	on	shi	ps	•	•	37
	3.2.2	The M <sub>s</sub> Temp	perature	and	То	•	•		•	•	•	•	• •	• •	•	•	43
	3.2.3	Quench Rate	e Depend	lence	••	•	•		•	•	•	•	• •	• •	•	•	46
	3.2.4	Effects of	Interst	itial	ls .	•	•	•••	•	•	•	•	•	•	•	٠	47
3.3	The ω	Phase			•••	•	•		•	•	•	•	• •	•		•	50
	3.3.1	Mechanics of	of Forma	tion	of	the	. 1	ωP	has	e	•	•	• •	•	٠	•	52
	3.3.2	Crystal Str	ructure	and (	Drie	nta	ti	מס	Re]	.at	10	nsl	hiŗ	s	•		55
	3.3.3	Athermal u	ú <b></b> -		• •	•	•	• •		•	•	•	• •		•	+	56
	3.3.4	Isothermal	ω		•••	•	•	••	•	•	•	•	• •	• •	٠	•	60
	3.3.5	Effects of	Interst	itial	ls.	•	•	••	•	•	•	•		•	٠	•	65
3.4	Relate	l Phenomena	• • • •	• •			•	••	•	•	•	•	• •	•		•	67
	3.4.1	Resistivity	v Measur	ement	s,	٠	•	• •	•	•	•	•	• •	•		•	68
	3.4.2	Vicker's Ha	ardness	Measu	irem	ent	8	••		•	•	•	• •	•	•		74
3.5	Result	of the Pre	esent In	vesti	gat	lon	-	Qu	enc	he	d .	A1:	Loy	s	•	٠	76
	3.5.1	Microstruct the Fast Wa	ures Re nter Que	sultinch	ing i	fro	•	••	•	•	•	•	• •	•	•		76
	3.5.2	Microstruct the Air Coc	ures Re 1 Quenc	sulti h .	ng i	Ero	n •		•			•	• •	•	•	•	80
	3.5.3	Microstruct	ures Re	sulti	ing i	Ero	m i	the	Fu	rn	aci	e (	Cod	1	*		86
	3.5.4	Resistiviti	es of t	he Qu	iencl	ned	A.	L10	ys	•	•	•	• •			•	89
	3.5.5	Vicker's Ha	rdness	Numbe	ers	•	•		•	•	•	•	• •	•	•	•	94
	3.5.6	Discussion	of the	Resul	.ts							•					99

а

3.6	Results of the Present Investigation - Quenched and Aged Alloys	107
	3.6.1 Microstructures of the 20 and 25% Nb Specimens	108
	3.6.2 Microstructures of the 30 and 35% Nb Specimen	112
	3.6.3 Effect of Intermediate Quench Rate	119
	3.6.4 Microstructures of the Directly Aged Alloys	121
	3.6.5 Vicker's Hardness Numbers	123
	3.6.6 Discussion of the Results	123
3.7	Summary	135
CHAPTE:	<u>R FOUR</u> - Stable Equilibria	138
4.1	Introduction	139
4.2	The α and β Phases	141
	4.2.1 The a Phase Crystal Structure and	1.60
	Orientation Relationships	142
	4.2.2 a Precipitate Morphology	144
	4.2.3 The β Phase Lattice Parameter	144
•	4.2.4 Diffusion in the $\alpha$ and $\beta$ Phases . , ,	148
4.3	Metallurgical Investigations of the Phase Diagram	155
	4.3.1 Effects of Interstitials	161
4.4	Phase Diagram Calculations	162
4.5	Results of the Present Investigation	168
	4.5.1 Microstructures Near the $\beta$ Transus	170
	4.5.2 X-Ray Diffraction Results	180
4.6	Discussion of the Results	186
4.7	Summary	193

vii

CHAPTER	R FIVE	-	Fut	ure	≥ V	lor	:k	ar	ıd	Fi	na	11	Su	Intri	ar	У	•	٠		۰	۰	٠	•	٠	•	•	194
5.1	Final	Su	imma:	ry	•	•	•	•	•	٠	٠	•	•	•	•	•	•	•	•	•	•	•	•	*	•	•	197
BIBLIO	GRAPHY	•	••	•	•	•	•	•	•	•	•,	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	199

APPENDIX A -	- Selected Area Diffraction Pattern Calculations	205
APPENDIX B -	- Electron and X-ray Diffraction Relative Intensity Calculations	210
APPENDIX C -	- Cubic Stereographic Projections	216
APPENDIX D -	- Equations of the Regular Solution Model	219

.

## LIST OF TABLES

.

# CHAPTER ONE

1.1	FERMILAB Specifications for	
	Interstitial Contents of 37.2% Nb	6
1.2	Atomic to Weight Percent Conversions	
	for the Alloys of the Present Study	6

# CHAPTER TWO

2.1	Impurity Analyses of the Etched Niobium and Titanium	•	#• 12.1	<b>.</b>	11
2.2	Melt Analyses of the Alloy Compositions	•	•		13
2.3	Impurity Analyses After the Vacuum Anneal	•	•	•	15
2.4	Tungsten Content	•	•	•	16
2.5	Impurity Analyses After a Furnace Cool	+			18

## CHAPTER THREE

3.1	Regular Solution Parameters Used in the Calculations of $T_0$ (from the literature)	•	•	•	•	45
3.2	d-spacings of the 20-FW Wire Specimen		•	•	•	81
3.3	d-spacings of the 20-AC Wire Specimen	•	٠	•	•	87
3.4	Resistivities of the Quenched Specimens		٠		•	93
3.5	Temperature Coefficients of the Resistivities	٠	•	•	•	93
3.6	.Vicker's Hardness Numbers of the Quenched Specimens		•	•	•	98
3.7	Second Phases in the Quenched Specimens				1	.00

3.8	ω Precipitate Dimensions as a Function of Aging Temperature	111
3.9	$\boldsymbol{\omega}$ Precipitate Dimensions as a Function of Aging Time	111
3.10	Vicker's Hardness Numbers of the Quenched and Aged Specimens	124
3.11	Vicker's Hardness Numbers of the Directly Aged Specimens	124
3.12	Second Phases in the Quenched and Aged Specimens	129
CHAPTEI	R FOUR	
. 4.1	Lattice Parameters of $\alpha$ -Ti	143
4.2	Effect of Interstitials on the $\alpha$ -Ti Lattice Parameters . (from FR076)	143
4.3	Lattice Parameter of g-Nb	145

.

4.4 Effect of Interstitials on the  $\beta$ -Nb Lattice Parameter . 145 (from the literature)

(from the literature)

x

#### LIST OF FIGURES

## CHAPTER TWO

2.1	Quench Rates Produced in This Study	• •		٠	٠	21
2.2	Specimen Used to Measure the Quench Rates	• •			•	22
2.3	Schematic of the Resistivity Rig	• •	,	•	•	25
2.4	Schematic of Specimen Origins in the Alloy Rods				•	32

## CHAPTER THREE

3.1	Structure of the $\alpha^{"}$ Martensite	•	•		•	38
3.2	Lattice Parameters of the $\alpha'$ and $\alpha''$ Martensites . (from the literature)	•	•	٠	•	40
3.3	The M <sub>S</sub> and T <sub>O</sub> Curves	•	•	•	•	44
3.4	Critical Quench Rates	•	•	•	•	48
3.5	The Pressure-Temperature Phase Diagram of Titanium (from BUN65)	•	•	٠	•	51
3.6	Schematic of the Mechanism of $\boldsymbol{\omega}$ Phase Formation .	•	*		•	53
3.7	Quench Temperatures from which Athermal $\omega$ has been Produced (from the literature)	•	•	•	*	58
3.8	Aging Temperatures at which Isothermal $\omega$ has been Produced	•		•	•	62
3.9	Resistivities as a Function of Alloy Composition . (from the literature)	•	•	•	•	69
3.10	Temperature Coefficients of the Resistivities (from the literature)	•	•	•	•	71

3.11	Vicker's Hardness Numbers
3.12	Quench Rates Produced in this Study
3.13	TEM Micrographs of the 20-FW Specimen
3.14	SAD Patterns of the AC Specimen Series
3.15	Dark and Bright Field Images of the 20-AC Specimen 85
3.16	Dark Field Images of the 20-AC and 20-FC Specimens 88
3.17	Resistivities vs Alloy Composition for the Quenched Specimens
3.18	po and <pre>po and <pre>o and <pre>po and <pre>compo and</pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre></pre>
3.19	Vicker's Hardness Numbers of the Quenched Specimens 97
3.20	Critical Quench Rates
3.21	Dark Field Images of the 20-AC-96/300 and 20-AC-96/400 Specimens
3.22	Bright Field Image of the 25-AC-288/400 Specimen 113
3.23	SAD Pattern and Bright Field Image of the 25-AC-96/450 Specimen
3.24	Low and High Magnification Images of the 30 and 35-AC-96/350 Specimens 116
3.25	Bright Field Images of the 30 and 35-AC-288/400 Specimens
3.26	Bright Field Image of the 35-AC-96/450 Specimen 120
3.27	Bright Field Images of the 20-AC-96/400 and 20-96/400 Specimens
3.28	Vicker's Hardness Numbers of the Quenched and Aged Specimens

	3.29	Vicker's Hardness Numbers of the Quenched and Aged Specimens	126
	3.30	Vicker's Hardness Numbers of the Quenched and Aged Alloys, and the Directly Aged Alloys . (as a Function of Alloy Composition)	127
	3.31	Schematic of the Lattice Matchings of the 8' and a Precipitates	134
	3.32	Phase Diagram of the Metastable Equilibria	136
CF	1APTE1	R FOUR	
	4.1	Lattice Parameters for & Phase Ti-Nb Alloys	147
	4.2	Nb Diffusion Coefficients in $\beta$ Phase Ti-Nb Alloys (from the literature)	150
	4.3	Diffusion Coefficient in & Phase Ti-Nb Alloys (as a Function of Temperature and Alloy Composition)	154
	4.4	Comparison of Diffusion in the $\alpha$ and $\beta$ Phases	156
	4.5	Experimental Phase Diagram Data	157
	4.6	Effect of Interstitials on the $\beta$ Transus (from KHA81)	163
ì	4.7	Comparison of Phase Diagram Data and Calculations (from the literature)	164
	4.8	Complete Low Temperature Phase Diagram Calculations (from the literature)	165
	4.9	Alloys and Aging Temperatures of the Present Investigation	169
	4.10	Diffusion Coefficients and Phase Diagram Calculations . (from the literature)	171
	4.11	LM Micrograph of the 30-960/500 Specimen	172

xiii

.

4.12	LM Micrographs of the 25-96/600 and 25-960/600 Specimens	174
4.13	LM Micrographs of the 35-960/500 and 35-960/600 Specimens	176
4.14	LM Micrographs of the 20 - 40% Nb Specimens Aged 960 Hours at 600C	177
4.15	LM Micrographs of the 25-288/700 and 30-288/700 Specimens	181
4.16	β Phase Lattice Parameters . as a Function of Composition and Aging Temperature	184
4.17	Experimental Data and Phase Diagram Calculations	189

•

.

.

xiv

CHAPTER ONE

## INTRODUCTION

#### CHAPTER ONE

#### INTRODUCTION

Titanium-niobium binary alloys form the basis of the superconducting industry world-wide. These alloys possess the ductility required to withstand true strains on the order of 10 to 15. (Such strains are typical of commercially produced superconducting wires which have optimized superconducting properties.) The aim of the wire fabrication process is to produce a very specific microstructure upon which the superconducting properties depend. This microstructure can be obtained through a judicious choice of processing parameters such as the drawing schedule, and the number, time and temperature of heat treatments.

Despite the technological significance of these alloys, there have been relatively few investigations of the phase transformations which can occur in them. There have been innumerable studies of various physical properties of these alloys, but most were done with little or no knowledge of the actual microstructures of the alloys investigated. This has resulted in confusion in the understanding of the interrelationships of properties and microstructures and has made it difficult to discern fact from supposition.

There are three factors which can have a marked effect on the microstructures and properties of these alloys. These are the thermal

history, the mechanical history and the interstitial contents. Most previous investigations of the properties of these alloys were poorly documented in these regards. Alloy composition is also an important factor, but this has been reported unambiguously in all but one of the earlier studies. Attention in the present study was focussed on the effects of thermal history, though several interstitial analyses were obtained in order to document the impurity levels.

The goal of the present study was to determine the stability limits of the phase equilibria in this alloy system, and to eliminate some of the confusion regarding the interrelationships of properties and microstructures. Alloy fabrication and specimen preparation techniques were carefully controlled and documented so that the results of the present study could be interpreted properly. Extensive microstructural investigations were performed in order to determine the nature of the phase transformations which took place. In several cases, correlations of the microstructures with physical properties were made as well.

The approach of this study was to investigate the phase equilibria over a broad range of alloy compositions. Eight alloys, in the range 20 to 70 at% Nb, were investigated. This approach enabled the observation of overall trends in the phase transformations, though it precluded in-depth studies of the specifics of the transformations. Many of the phase transformations observed are deserving of further investigation which time and material did not permit. Thus, the

results of the present study may serve as a foundation for future investigations.

This study was divided into two complementary investigations of the phase equilibria in which the thermal histories of the alloys were varied. Each specimen received a recrystallization anneal at 1000C immediately before quenching or isothermal aging. This provided a point of reference for all specimens in this study. The metastable equilibria in this alloy system were studied in specimens which had been quenched and in those which had been quenched and aged. The stable equilibria were investigated in specimens which had been directly aged.

In any fundamental study of phase transformations it is important that the alloys used are of the highest possible quality, i.e. have very low interstitial contents. At the industrial level, however, economic concerns force a trade-off between purity and cost. While the present study was intended to be a basic investigation of phase transformations, it was also desired that its findings be pertinent to industrially used alloys. For this reason, commercially pure titanium was used in this study as one of the starting materials. Use of a more pure grade of titanium might have altered some of the results of this study, but also might have limited their applicability. In defense of this, it should be noted that the FermiLab specification for superconductor wire, to which most of the world's Ti-Nb superconductor is manufactured, is fairly restrictive. The FermiLab specifications are given in Table 1.1 (recently the oxygen limits were lowered to 800 wppm).

The outline of this thesis is as follows. In Chapter 2 are discussed the techniques used in this study. Chapter 3 is concerned with the metastable phase equilibria, Chapter 4, the stable equilibria. Chapter 5 contains a discussion of work which may be pursued in the future, as well as a final summary. Several points of reference are given in the Appendices. There is no all-encompassing literature review in this thesis. Instead, it has been divided according to the contents of each chapter. This was done to keep the material fresh in the reader's mind, and to facilitate the publication of this work.

#### 1.1 Nomenclature

All compositions given in this thesis are in atomic percentages. The alloys of this study are designated only by the atomic percentage of niobium in a given alloy. In the presentation of the literature, other alloy systems are discussed. Again, the compositions of these alloys are given in atomic percentages, even though the original work may have used weight percentages. Commercially, Ti-Nb alloys are designated by weight percentage of titanium. To facilitate comparisons between the alloys of this study and those of the superconductor industry, the alternate designation for the alloys of this study are given in Table 1.2.

## TABLE 1.1

FERMILAB Specifications for Interstitial Contents of 37.2% Nb (46.5wt% Ti)

	wppm	appm
С	200	1070
N	150	688
0	1000	4017
H	20	1275

## TABLE 1.2

Atomic to Weight Percent Conversions For the Alloys of the Present Study

at% Nb	wt% Ti
20	67.3
25	60.7
30	54.6
35	48.9
40	43.6
50	34.0
60	25.6
70	18.1

.

\*\*

Interstitial analyses are given in atomic parts per million, as well as the customary weight parts per million. Atomic parts per million were used because it is believed that they give a more accurate description of the impurities in the alloys. This makes alloys appear less pure than if wppm were used, which was exactly the intent.

The specimens of the present study are identified by four parameters. The first is the composition of the alloy, in atomic percent niobium. Second comes a two letter mnemonic for the type of quench the specimen received. Lastly comes the time, in hours, and the temperature, in degrees Celsius, of any heat treatment. Examples of this identification system are: 20-FW (20% Nb alloy which was fast water quenched from 1000C to room temperature); 30-AC-96/400 (30% Nb alloy, air cooled to room temperature, then heat treated for 96 hours at 400C); 50-288/500 (50% Nb alloy recrystallized at 1000C then aged at 500C for 288 hours with no intermediate room temperature quench). For future reference, the heat treatment times used in this study were 96 hours (4 days), 288 hours (12 days), and 960 hours (40 days). CHAPTER TWO

# SPECIMEN PREPARATION AND EXPERIMENTAL TECHNIQUES

.

b.

\*

#### CHAPTER TWO

#### SPECIMEN PREPARATION and EXPERIMENTAL TECHNIQUES

#### 2.1 Introduction

A major concern of this study was to ensure that the phase transformations that were observed were not affected by interstitial contamination. If present at sufficient levels, interstitials could modify the phase transformations that otherwise would occur in pure alloys. The presence of interstitials also could cause transformations that would not occur in pure alloys, e.g. the precipitation of oxides or hydrides.

All of the alloys used in this study were prepared at the UW. Great care was taken to ensure that the alloys were homogeneous and that contamination was held at a minimum. Several analyses of the alloys were obtained in order to verify their quality. All chemical analyses were performed by Teledyne Wah Chang-Analytical Services, Albany, OR.

Interstitial contamination can occur during the preparation of the specimens used for microstructural characterization. The techniques developed during the preliminary investigation of this system were shown to produce high quality specimens and were used throughout this study.

#### 2.2 Alloy Fabrication

The raw materials used to prepare the alloys were 3mm rods of niobium and 1.6mm rods of commercially pure titanium. To remove any surface oxidation, the rods were etched in a solution of 13% HF, 20% HNO<sub>3</sub> and 67% H<sub>2</sub>O. After a moderate etch, the rods were dropped quickly into a methanol/dry ice bath to stop etching. The rods then were rinsed with fresh methanol twice, dried, and stored in a desiccator until needed. Interstitial analyses of the etched rods are given in Table 2.1. (Table 2.1a gives the analyses in wppm.)

Alloy ingots were melted in an arc melter with a tungsten electrode and a water-cooled copper base. After loading the niobium and titanium rods, the arc melter was evacuated ( $\leq$  20mTorr) and back-filled with pre-purified (as supplied by the manufacturer) argon five times. Before the rods were first melted, the arc was moved over the entire surface of the copper base to remove any adsorbed water vapor. A titanium button was melted after this to getter the argon atmosphere. This procedure was repeated before each melt of the alloy ingot.

The ingot was melted and inverted at least 10 times in a square depression (the ingot could be inverted without opening the arc melter). The repeated melting and inverting of the ingot allowed the operator to verify that complete melting of the niobium rods had occurred, assuring a macroscopically homogeneous ingot. The ingot

# TABLE 2.1

Impurity Analyses of the Etched Niobium and Titanium

	C	N	0	<u>H</u>
Niobium Titanium	<232	212 143	348 1881	<460 1138
Errors		10%	5%	10%

All values in appm

# TABLE 2.1a

Impurity Analyses of the Etched Niobium and Titanium

	C	N	0	<u><u> </u></u>
Niobium Titanium	<30	32 42	60 630	<5 24
Errors		10%	5%	10%

All values in wppm

then was shaped into a cylinder roughly 1cm in diameter by 10cm long. This ingot could be supported by the copper base in such a way that cooling was not very efficient. In this way the ingot could be heated fairly uniformly to just below the solidus, effecting a very high temperature homogenization heat treatment. The ingot was rolled over and this process repeated several times, producing a homogeneous ingot. (SEM analyses of several test ingots verified that this process produced homogeneous ingots.)

During melting some material always was lost. For this reason, each ingot was weighed after melting to monitor the change in overall composition. The greatest deviation from the assumed composition would occur if the material lost was either all niobium or all titanium. This worst-case error was computed for each ingot. The results are shown in Table 2.2. (As there were two ingots of each alloy, the results given in Table 2.2 are averages.) It can be seen that the greatest possible error was .54% Nb; most errors were significantly smaller.

After removal from the arc melter, the ingots were homogenized again to remove any residual microscopic inhomogeneities. Each ingot was wrapped in niobium foil and placed in a silica tube with several pleces of titanium rod. The tubes were evacuated ( $\leq$  10mTorr) and back-filled with pre-purified argon five times before sealing at a pressure of 150 Torr. The ingots were homogenized at 1300C. The 50, 60 and 70% Nb alloys were homogenized for 24 hours; all others were homogenized for 8 hours. Longer times were used for the high niobium

TAB	LE	2	2

Melt Analyses of the Alloy Compositions

Nominal	Actual	Worst-Case	Errors
20	20.00	+.005	005
25	25.01	+.015	025
30	30.03	+.075	095
35	35.00	+.18	165
40	39.99	+.215	165
50	49.98	+.325	165
60	60.00	+.305	1
70	70.06	+.54	12

All percentages in atomic percent Nb

alloys because diffusion is more difficult in these alloys. Following homogenization, the ingots were quenched by breaking the tubes under water. (This was done to prevent the precipitation of the  $\omega$  phase which could have made swaging of some of the ingots impossible.)

The homogenized ingots were swaged to 3mm rods without difficulty. The area reduction of each swaging pass was about 20%. After swaging, the rods were cleaned several times with acetone to remove the swaging lubricant, sanded, and then etched in the same solution as before.

Post-factum, it was discovered that the homogenization quench introduced significant quantities of hydrogen into the alloys. To remove this hydrogen, the 3mm rods were vacuum annealed at 800C. The annealing time was 3 hours, during which time the vacuum was  $^{7}x10^{-6}$  Torr. The vacuum for the 20 and 25% Nb alloys, however, was only  $^{-1}x10^{-5}$  Torr. The furnace was turned off and allowed to cool before opening after the anneal. A section of each alloy was analyzed for impurities after this anneal. The results are shown in Table 2.3. (Table 2.3a gives the results in wppm.)

To verify that there had been no tungsten contamination during arc melting, a section of each alloy was analyzed for tungsten. These results are shown in Table 2.4.

The alloys described in Tables 2.2 to 2.4 were those used in all subsequent investigations of the phase transformations. The actual compositions of the alloys were in excellent agreement with the nominal compositions. The errors shown in Table 2.2 are as

## TABLE 2.3

.

# Impurity Analyses After the Vacuum Anneal January 1983

At% Nb	C	<u>N</u>	0	H	Total
20	755	445	2903	1068	5171
25	785	193	3019	993	4990
30	865	257	3821	546	5489
· 35	739	181	2774	692	4386
40	656	211	1930	456	3253
50	526	186	1580	418	2710
60	746	203	1634	<371	2954
70	791	249	2425	<393	3858
	1	11 values	in appm		

## TABLE 2.3a

# Impurity Analyses After the Vacuum Anneal January 1983

At% Nb	<u> </u>	N			H	Total
20	160	110		820	19	1109
25	160	46		820	17	1043
30	170	59		1000	9	1238
35	140	40		700	11	891
40	120	45		470	7	642
50	90	37		360	6	493
60	120	38	+	350	<5	513
70	120	44		490	<5	659

All values in wppm

# TABLE 2.4

÷

.

Tungsten Contents of the Alloys

At% Nb	appm W
20	<3
25	4
30	<3
35	26
40	4
50	4
60	167
70	8

.

.

pessimistic as possible -- the actual deviations from the nominal compositions were much less. Table 2.4 shows that tungsten contamination from the arc melter was negligible. The anomalously high value for the 60% alloy most likely was due to the difficulty encountered in the melting of that particular alloy.

It is difficult to determine the level at which interstitial impurities influence the phase transformations in the Ti-Nb system. Most phase transformation studies reported in the literature give an insufficient accounting of interstitials. While the present study has attempt to determine the effects of interstitial made no contamination, it can provide a benchmark for later studies. To this end, the analyses of the four important interstitials have been given in Table 2.3. The total impurity content can be seen to range from .27% to .55%. This may appear to be unacceptably high for a fundamental study such as this, but it should be reinforced that these percentages, not reported weight are atomic the customarily percentages. (The same range in weight percentages is .05% to .12%.)

Due to the time interval between the date of the analyses shown in Table 2.3 and the last heat treatments, the alloys were analyzed again. The results are shown in Table 2.5. (Table 2.5a gives the analyses in wppm.) These alloys had been annealed at 1000C and then furnace cooled to room temperature as part of the quench rate studies. The variations can be attributed to the differences in the two original ingots of each alloy and to the errors inherent in such analyses.

#### TABLE 2.5

#### Impurity Analyses After a Furnace Cool March 1985

At% Nb	C	<u>N</u>	0	_ <u>_</u> H	Total
20	755	486	2835	844	4920
25	834	261	3645	993	5733
30	1120	223	3860	607	5810
35	687	- 186	2380	567	3820
40	602	239	2423	652	3916
50	701	240	3158	418	4517
60	684	192	2708	<371	3955
70	725	413	2870	<393	4401

All values in appm

## TABLE 2.5a

# Impurity Analyses After a Furnace Cool March 1985

At% Nb	С	N	0	H	Total
20 25 30 35 40 50 60	160 170 220 130 110 120 110	120 62 51 41 51 48 36	800 990 1010 600 590 720 580	15 17 10 9 10 6 <5	1095 1239 1291 780 761 894 731
70	110	73	580	<5	768

All values in wppm

#### 2.3 Heat Treatment Technique

The phase transformations that were studied in this alloy system occurred between 1000C and room temperature. These transformations could take place either during isothermal aging or during quenching. They also could be affected by interstitial contamination. Thus it was necessary that the heat treatment technique not only prevent any further contamination of the specimens, but also minimize the complications due to competing transformation reactions.

The materials used for all heat treatments were the 3mm rods described in section 2.2. For heat treatment, a 25 or 50mm length was cut with a low speed diamond saw from a 3mm rod. This short rod was ultrasonically cleaned, twice in acetone, twice in methanol, to remove any cutting fluid. The rod was not etched before heat treating.

The cleaned rod was placed in a silica tube with two titanium getters. The tube was evacuated ( $\leq 10$ mTorr) and back-filled with pre-purified argon five times and then sealed at a pressure of  $\leq 10$ mTorr. From the manufacturer's analysis of the argon, it was calculated that the impurity partial pressures of this atmosphere at room temperature were:  $P_{N_2} = 1.5 \times 10^{-7}$  Torr,  $P_{O_2} = 6.5 \times 10^{-8}$  Torr,  $P_{H_2} = 9 \times 10^{-8}$  Torr. (This translates to "3x10" atoms for each of these impurities.)

The sealed rods were placed in a 1000C furnace for a solution anneal and recrystallization. This anneal was necessary for two

reasons. First, it removed any transformation products, e.g.  $\omega$  in the high titanium alloys, that might have formed during cooling after the vacuum anneal. Second, it removed the cold-work introduced during swaging. (Swaging produced a true strain of ~2 in the 3mm rods.) Light metallography showed that the 20 - 35% Nb alloys were well recrystallized after 8 hours at 1000C, while the high niobium alloys (40 - 70% Nb) required 24 hours.

During this anneal the titanium getters slowly vaporized, coating the inside of the tube, and the alloy rod, with titanium. As the titanium evaporated, it thoroughly gettered the argon atmosphere. Using the diffusion coefficients of the alloys, it was calculated that the titanium which coated the rod would have diffused less than  $10\mu m$ into the rod.

After recrystallization, the specimens received one of three thermal treatments. Some were quenched to room temperature from 1000C. Others were quenched to room temperature and then isothermally aged. The third group of specimens was placed directly into another furnace at the desired aging temperature. Following isothermal aging, the tubes were quenched to room temperature by breaking them under water.

#### 2.3.1 Quenching

The three different quench rates used in the present study are shown in Figure 2.1. The fast water (FW) quench was produced by



FIGURE 2.1 Quench rates produced in this study (Measured using the specimen shown in Figure 2.2)


FIGURE 2.2 Schematic of the specimen used to measure the quench rates in this study

quickly taking a tube from the furnace and breaking it under water. Removing a tube from the furnace and placing it on a table resulted in an air cool (AC) quench. (It should be noted that air cooling was equivalent to taking a tube from the furnace and quenching it in water, but not breaking it.) The slowest quench, furnace cooling (FC), was produced by turning off the furnace and allowing the specimen to cool with the furnace.

The fast water quench did not always produce a uniform quench. When an evacuated tube was broken under water, water was sucked into the tube, bringing it into contact with the hot alloy rod. Initially, this vaporized the water, which in turn blocked the passage of more water if the quartz tube had not been completely shattered. This produced a momentary reduction in cooling. This effect could be minimized by ensuring that the tube was broken near the middle of the alloy rod.

The quench rates shown in Figure 2.1 were measured using the specimen shown schematically in Figure 2.2. The specimen was a 64mm length of alloy rod through which a #78 (.41mm) hole had been drilled. The junction of a Pt/Pt-13%Rh thermocouple was placed in the center of the rod. (Initially, Chromel/Alumel thermocouple wires were used; however, it was found that the thermocouple wires wetted the alloy rod at 1000C and completely dissolved.) The leads were placed in shallow grooves in the sides of the rod, fed through a very fine alumina insulator, and then out one end of the tube. This end was sealed with epoxy. After the epoxy had hardened, the tube was sealed under

vacuum, as described above, through the other end. Cooling curves were recorded on a chart recorder.

### 2.4 Resistivity Measurements.

Measurements of the resistivities of several alloys were made for two reasons. They provided an indirect measure of the occurrence of phase transformations and they provided needed data to the superconductivity community. Resistivities were measured at room temperature (~295K), 77K, and just above the superconducting transition temperature,  $T_c$  (~10K).

The device used for measuring resistivities was based on a four point measurement technique. Each of four specimens was held as shown schematically in Figure 2.3. The specimens were 50mm lengths of heat treated 3mm rods. The current leads held the specimen tightly against the fixed voltage taps, which were stainless steel knife edges. The gauge length was about 25mm. From an analysis of the factors that could contribute to errors in the measurements, it was calculated that the relative errors in the resistivities were .6%.

## 2.5 Light Metallography

Light metallography (LM) provided direct observation of the products of a phase transformation at a coarse scale. The entire cross-section of a 3mm rod could be studied to verify that a



FIGURE 2.3 Schematic of the apparatus used to measure resistivities between room temperature and 4.2K

transformation had occurred uniformly throughout the rod (this was necessary for the TEM and XRD evaluations to be of value). The specimens polished for LM also were used for microhardness measurements.

Specimens for LM were cut from one end of heat treated rods with a low speed diamond saw. The specimens were approximately 3mm long. Each was mounted in bakelite or diallyl phthalate such that the freshly-cut end was exposed. The specimens were polished using the technique of Paul Danielson at Wah Chang. After polishing, the specimens were etched in a solution of 2% HF, 3%  $HNO_3$ , and 95%  $H_2O$ . This was a slow etch which produced good microstructural detail. Microhardness measurements were made on polished, unetched specimens using a 100g load.

This technique ensured that the LM specimens were representative of the pure, bulk alloys. Calculations using the impurity diffusion coefficients showed that any contamination which may have occurred during heat treatment would be limited to a narrow surface layer in the rods. For example, during a 100 hour heat treatment at 500C, nitrogen would have diffused into the rod ~10µm, oxygen, ~60µm. Because the polished face of the specimen was not an external surface, only the perimeter would have been susceptible to contamination. On examination, no contamination layer was ever observed in a specimen. In addition to being free from contamination, the polished face also was representative of the bulk alloy as it had been cut from the interior of the rod. 2.6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) also provided direct observation of the products of a phase transformation, though at a much finer scale than LM. TEM images provided information about the nucleation behavior and morphology of precipitates, while selected area diffraction (SAD) patterns yielded information about crystal structures and orientation relationships with the matrix. Conventional SAD, however, cannot be used to determine lattice parameters as accurately as x-ray diffraction. The TEM used in this investigation was a JEOL 200CX-II operated at 200keV.

TEM specimens were cut from the mid-section of a heat treated length of 3mm rod with a low speed diamond saw. (The end of the rod was used for LM as noted above.) The disks were ultrasonically cleaned twice in acetone to remove the cutting fluid. The specimens, which were ~.7mm thick, were ground on both sides with 320 grit SiC abrasive paper until they were ~.2mm thick. The disks were ultrasonically cleaned again in methanol.

TEM foils were prepared in a twin jet electropolisher commercially produced by E. A. Fischione. A solution of 2% HF, 5%  $H_2SO_4$ , 93% methanol was used at -40 to -50C. The polishing current was ~35mA. Immediately upon perforation, the foil was removed from the solution and thoroughly rinsed with methanol. The foils were stored in air.

This specimen preparation technique also ensured that the observed phase transformations were representative of the pure, bulk alloys. This is particularly important for TEM specimens because the area examined is extremely small. For comparison, the TEM specimens of most studies are punched from a thin sheet, and then heat treated and electropolished.

An inevitable consequence of electropolishing Ti-Nb alloys is the introduction of hydrogen from the electrolyte. Even though they were polished at -50C in a very dilute solution of HF, the foils were susceptible to contamination because of their extreme thinness. Interstitial hydrogen can produce two effects in a TEM specimen -- it can remain in solid solution, expanding the BCC lattice, or it can lead to the precipitation of hydrides. Nothing could be done to avoid examination of the material which may have been swollen because such material was impossible to identify. Hydride precipitation, though infrequently observed, was easily recognizable. Because hydrides formed at the edge of the hole in a TEM foil, observations were made in somewhat thicker regions of the foil.

2.7 X-ray Diffraction

X-ray diffraction measurements (XRD) complemented the TEM crystal structure information. Accurate lattice parameter measurements and additional crystal structure data were obtained with x-ray techniques. Powder for x-ray specimens was filed from the heat treated rods after the TEM specimens had been cut from them. Each rod was mounted in an automatic filing device which fed the rod at a rate of ~40µm/min onto a carbide rotary file rotating at ~30,000rpm. The rod was slowly rotated at ~.05rpm as it was fed onto the file. Because most heat treated Ti-Nb alloys caused some wear of the file, a fresh section of the file was used for each rod. This minimized the amount of file material that became part of the powder.

The powder was prepared for annealing after filing. Only that powder which passed through a 200 mesh sieve (i.e.  $\langle 75\mu m \rangle$ ) was annealed. A thin piece of niobium foil was rolled into a cylinder and one end folded over. Into this was placed a titanium rod and the sieved powder (the titanium rod acted as a getter during the anneal). The other end then was closed and the cylinder put in a silica tube. The tube was sealed at a vacuum of  $\leq$  10mTorr in the same manner as described before.

It was necessary to anneal the powders to remove the strains introduced by filing. Though the powder particles had a high surface to volume ratio, making them susceptible to contamination during the anneal, unannealed powders produced unuseable diffraction patterns. An extensive series of experiments demonstrated that the technique used did not introduce significant contamination (see MOF82). Each powder was annealed at the same temperature at which the parent rod had been heat treated in order to preserve the microstructure produced during the heat treatment. The annealing time depended on the

annealing temperature. The tubes were quenched by dropping them in water, but not breaking them.

The XRD specimens were prepared from the annealed powders. The powders were sieved with a 400 mesh sieve. The powder that passed through this sieve (<38µm) was discarded because it had a higher impurity content due to its very fine nature. The retained powder was poured into a .3mm capillary for x-raying.

The diffraction patterns were recorded on film in a 114.6mm diameter Debye-Scherrer camera. Nickel-filtered copper radiation was used and the exposure time was 8 hours for a filament current of 20mA.

Lattice parameters were determined by extrapolation on a Nelson-Riley plot. The values used for the wavelengths in the calculations were: Ka =.154171nm; Ka<sub>1</sub> =.154044nm; Ka<sub>2</sub> =.154426nm. Only those diffraction lines with Bragg angles  $\geq 45^{\circ}$  were used in the extrapolations. This was done primarily because the high angle lines were less susceptible to measurement errors, the Nelson-Riley extrapolation eliminating the errors due to x-ray absorption. Typically, the highest angle BCC line occurred at ~85°.

## 2.8 Summary

The specimen preparation techniques described in this chapter were developed with particular emphasis placed on the minimization of interstitial contamination. Great care was taken to maintain the high quality of the alloys throughout this study.

The only alloys used in this study were described in section 2.2. Two alloys of each composition were melted and all alloys were prepared within a short time span. This ensured uniformity in fabrication. Several impurity analyses were performed on the alloys to monitor their quality during and after processing.

One length cut from the 3mm stock rod provided all the specimens scrutinized for a given thermal treatment. LM, TEM and XRD all were performed on specimens from the one length (see Figure 2.4). This eliminated the chance of conflicting results due to processing errors.

Three direct observation techniques, and two indirect techniques were used to study the phase transformations. No one technique could provide all the information desired. Together, the use of these techniques yielded a more complete understanding of the phase relationships in this alloy system.



FIGURE 2.4 Schematic of the specimen origins from a 25mm length of an alloy rod

CHAPTER THREE

÷

# METASTABLE EQUILIBRIA

a.

### CHAPTER THREE

#### METASTABLE . EQUILIBRIA

## 3.1 Introduction

The nature of the equilibrium phase diagram is such that above 882.5C all Ti-Nb alloys are single-phase  $\beta$ . At lower temperatures, the kinetics of the decomposition of the  $\beta$  phase to the stable two-phase mixture are sluggish, allowing the formation and observation of metastable phases.

The metastable phase transformations observed in the Ti-Nb alloy system are similar to those observed in alloys of titanium with other transition elements. The Ti-Nb and Ti-Ta systems possess the smallest differences in the atomic volumes of the constituents, being less than 2%. When coupled with the fact that the d-shell electronic structure of niobium is different from that of vanadium and tantalum, one finds that the Ti-Nb system is unique among the titanium-based alloys. Perhaps due to these factors, the metastable equilibria in this system also are more complicated.

Three metastable phases in this system have been identified by several independent investigations. They are  $\alpha$ , a hexagonal close-packed martensite,  $\alpha$ ", an orthorhombic martensite, and  $\omega$ , a hexagonal modification of the body-centered cubic matrix. The composition limits of the two martensites do not overlap, although those of  $\alpha$ " and  $\omega$  do.

A fourth metastable phase,  $\beta$ , is the result of a  $\beta$  phase miscibility gap. This phase has been well documented in other alloy systems, but has not been identified unambiguously in the Ti-Nb system.

This part of the present study was begun in an attempt to establish the limits of stability of the metastable phases. It also was desired to correlate the metastable microstuctures with two of the physical properties of these alloys. The microstructural results were found to be in general agreement with the data of the literature. During the course of this study, however, several new results were obtained.

Several factors affect the metastable equilibria in the Ti-Nb alloy system. The effect of alloy composition has been established in the literature. The effect of quench rate on alloy microstructure has been investigated by others, but only in a qualitative fashion in a few alloys. (The effect of quench rate on the physical properties of these alloys has received no attention.) The effect of quenching prior to isothermal aging has not been studied previously. The time and temperature of isothermal heat treatments are also important factors. The effects of all of the above factors were investigated in the present study.

Not studied in this investigation, but of importance, were the effects of interstitial content. Very few of the studies in the

literature reported the interstitial contents of their alloys. Instead, what were reported customarily were the impurities in the pure titanium and niobium. Without impurity analyses of the alloys actually studied, the quality of the alloy fabrication techniques can not be assessed and the impurity levels in the alloys only estimated. Interstitial analyses for the alloys of the present study were given in section 2.2.

This chapter is laid out in the following manner. A review of the pertinent literature is given first. Interspersed throughout this review are comments related to previous authors' interpretations or to conflicting results. Following the literature review are the results of the present study which have been divided into two sections -- the first pertaining to quenched alloys, the second, to quenched and aged alloys. The microstructures resulting from the various thermal treatments and their effect on resistivities and microhardnesses are reported and then discussed in each section. The final summary of this chapter presents an overview of these results in the form of a semi-quantitative metastable phase diagram.

# 3.2 Martensitic Phases

Titanium-miobium alloys have been shown to exhibit two forms of martensite,  $\alpha'$  and  $\alpha''$ . These martensitic phases have been found in other alloys of titanium with transition elements as well (for examples see BR066 or COL84). The  $\alpha'$  martensite forms in alloys with

low miobium concentrations, a" at higher concentrations. The  $\alpha^{-}/\alpha^{"}$ "boundary" has been reported to occur at 7% Nb (BAG59), between 5 and 10% Nb (BR066, JEP70), and at 11% Nb (MOR73). The high temperature  $\beta$ phase is retained on quenching in alloys in which the composition is between 20 and 25% Nb (BR066), greater than 26% Nb (HIC69), or >28% Nb (MOR73).

3.2.1 Crystal Structures and Orientation Relationships

The structure of the  $\alpha$  martensite is HCP (BR066, JEP70, MOR73). The lattice parameters of  $\alpha$  are the same as those of  $\alpha$  and do not vary appreciably with niobium content.  $\alpha$  obeys the BCC/HCP Burger's orientation relationships which are:

> (0001) α<sup>-</sup> || (011) β <1120> α<sup>-</sup> || <111> β

The transformation of  $\beta$  to  $\alpha$  can be accomplished by (COL84):

a 10% contraction along [100] which corresponds to [2110]

a 10% expansion along [011] which corresponds to [0110]

a 1% expansion along [011] which corresponds to [0001]

The structure of  $\alpha$ " is shown in Figure 3.1 (from MOR73).  $\alpha$ " is C-centered orthorhombic with a space group of Cmcm (BAG59, BR066, HAT68, JEP70, MOR73). The atom positions in  $\alpha$ " are: (0, 0, 0), (0, -2y, 1/2), (1/2, 1/2, 0), (1/2, 1/2-2y, 1/2). From intensity measurements of x-ray diffraction patterns, it has been estimated that

37



FIGURE 3.1 Structure of the a" martensite showing how it relates to the HCP and BCC structures (from MOR73)

y is between .19 (MOR73) and .2 (BR064), but may vary with composition (MOR73).

The orientation relationships of the two martensites are similar. The orientation of  $\alpha^{\prime\prime}$  with respect to  $\beta$  was shown to be (HAT68, MOR73):

[001] α" || <110> β [100] α" 2-3° from <00Ī> β [010] α" 2-3° from <Ī10> β

The  $\alpha^{"}$  structure may be viewed as a transition between the HCP structure of  $\alpha'$  and the BCC structure of  $\beta$ . By adjusting y, b and c, one can produce all three structures (MOR73). For example, an HCP structure is obtained when y = .1667 and b/a =  $\sqrt{3}$  (the ideal c/a for HCP is  $\sqrt{8/3}$ ). A BCC structure is obtained when y = .25, b/a =  $\sqrt{2}$ and c/a =  $\sqrt{2}$ .

The lattice parameters of the two martensites are shown in Figures 3.2a, b and c. These figures demonstrate the transitional nature of  $\alpha$ ". With the exception of the data for the 25 - 28% Nb alloys, the  $\alpha$ " lattice parameters in each figure fall fairly close to a straight line. It is interesting to note that the extrapolations of each  $\alpha$ " lattice parameter intersect the HCP and BCC values at about 7.2 and 30.6% Nb, respectively. This would seem to indicate the compositional limits of  $\alpha$ " formation.

The data of section 3.2.2 show that  $M_S$  is below room temperature for alloys with niobium compositions of more than about 25%. As Morniroli and Gantois (MOR73) did not indicate that any of their



FIGURE 3.2a The a lattice parameter of the martensites (from the literature)



FIGURE 3.2b The b/a lattice parameter of the martensites (from the literature)



FIGURE 3.2c The c/a lattice parameter of the martensites (from the literature)

diffraction measurements were performed below room temperature, their lattice parameter data for the 25 - 28% Nb alloys are suspect.

3.2.2 The Ms Temperature and To

The M<sub>8</sub> temperature as a function of composition is shown in Figure 3.3. The transformation temperatures were observed as breaks in cooling curves. To effect fast quench rates, thin specimens were used, typically between .13 and .5mm in thickness. A thermocouple was spot welded to the specimen in order to measure its temperature accurately. (It is interesting to note that Chromel/Alume1 thermocouples were used in several studies (DUW53, SAT60, KAN63). In section 2.3.1 it was reported that Chromel/Alumel thermocouples dissolved when in contact with Ti-Nb alloys at 1000C.) As the niobium content of an alloy was increased, the amount of  $\beta$  phase material which transformed to martensite decreased. This resulted in a diminution of the thermal arrest signal, which eventually became too weak to measure below "300C (DUW53, SAT60). A reasonable extrapolation of the M8 data indicates that an alloy of ~32% Nb would have an Ms of OK. This limiting composition for the formation of a" is in good agreement with the a" lattice parameter extrapolations of Figures 3.2.

The thermal arrest technique does not enable one to determine the nature of a transformation, only that one took place. Flower, et al. (FLO82) noted that in order for there to be an  $\alpha^{-1}/\alpha^{-1}$  "transition",



FIGURE 3.3 The M<sub>S</sub> data and calculations of T<sub>o</sub> (from the literature)

# TABLE 3.1

Regular Solution Parameters for  $T_{\rm O}$  Calculations

$\Delta G_{T1}^{\beta \neq \alpha} = -1050 + .91T$	(KAU70)
$\Delta G_{\rm Nb}^{\beta + \alpha} = 1500 + .8T$	(KAU70)
$A = 3125, B \approx 3125$ $A = 2438, B \approx 1243$	(KAU70) (MUR84)

All values in cal/mole

there must exist two  $M_S$  curves, one for each martensite, and that they must cross. There is too much scatter in the data, however, to verify this.

Calculated  $T_0$  curves also are shown in Figure 3.3. ( $T_0$  is the temperature at which the free energies of the  $\alpha$  and  $\beta$  phases are equal.) These are regular solution calculations based on the parameters shown in Table 3.1.  $M_s$  should always fall below  $T_0$ . As can be seen, this is not always the case, particularly for the calculations of Murray (MUR84).

There are two possible explanations for this discrepancy. It is quite possible that the parameters used in the calculations are incorrect. The parameters of Murray (MUR84) were derived by modelling the experimental data for the equilibrium phase diagram (see section 4.4). These data are subject to some uncertainty (see Chapter 4). It is also very likely that the M<sub>S</sub> specimens, due to their thinness, became contaminated during the heating and quenching processes. This latter point will be discussed further in section 3.2.4.

# 3.2.3 Quench Rate Dependence

The quench rate sensitivity of Ti-Nb alloys varies with alloy composition, with the niobium-rich alloys being more sensitive (JEP70). The study by Jepson, et al. demonstrated two interesting points in this regard. First, it was found that there was a sharp drop in M<sub>S</sub> for a given alloy when the quench rate exceeded a certain

value. Quench rates faster than this did not cause  $M_S$  to vary. The drop in  $M_S$  was negligible for 0 and 5% Nb alloys, about 20C for a 10% Nb alloy, and for a 17.5% Nb alloy had increased to about 125C. The cooling rates at which this drop occurred are shown as the lower curve in Figure 3.4.

The second interesting point is that it was found that the martensitic transformation could be completely suppressed in all alloys using very high quench rates. These critical quench rates were found to vary with composition and are shown as the upper curve in Figure 3.4. Those alloys which retained the  $\beta$  phase on quenching could be transformed readily to martensite with deformation. The three regions in Figure 3.4 were labeled by Jepson, et al. M<sub>B</sub> is relatively independent of quench rate for quench rates and alloy compositions between the curves (DUW51, JEP70).

At high miobium concentrations and slow quench rates, it becomes possible for the  $\omega$  phase to form during quenching. Morniroli and Gantois (MOR73) reported that in an 11.4% Nb alloy, water quenching produced  $\alpha$ ", while slow cooling yielded  $\omega$  precipitates. A similar effect was observed in a 20.7% Nb alloy (HAT68).

# 3.2.4 Effects of Interstitials

The effects of interstitial elements in solution are two-fold. Interstitials may result in an elevation or depression of  $M_s$ , and/or they may alter the crystal structure of the martensite. While no



FIGURE 3.4 Critical quench rates for Ti-Nb alloys (from JEP70)

investigation has been made of these effects in the Ti-Nb system, some information may be deduced from the available data.

Carbon, nitrogen and oxygen in solution can lead to an elevation Khaled, et al. (KHA81) have shown theoretically that these of Ms. impurities lower the free energy of the a phase in titanium-based (This is corroborated by the Ti-C, Ti-N and Ti-O phase alloys. diagrams (HAN58).) This results in an increase in  $T_{\rm O}$  and, therefore, Analysis of the specimen preparation techniques used in the Me. studies cited in sections 3.2.2 and 3.2.3 indicates that interstitial contamination is to be expected in the thermal arrest specimens. In addition, the specimens could have become further contaminated during the course of the Ms experiments themselves. To illustrate, using the impurity diffusion data for niobium (FR076), one finds that oxygen could diffuse to the center of a .13mm specimen in ~2.5 minutes at 1000C (38 minutes would be required for a .5mm specimen). Shorter times or lower soaking temperatures would result in a contamination layer on the surface of the specimen. Duwez (DUW51) observed transitions between 905 and 960C in pure titanium which were attributed to such contamination.

Examination of the Ti-H phase diagram (HAN58) shows that hydrogen in solution stabilizes the  $\beta$  phase over the  $\alpha$  phase. To effect extremely fast quench rates, Jepson, et al. (JEP70) chemically thinned their specimens to .05 ~ .13mm in an HF solution. This would be expected to result in significant hydrogen contamination of the specimens (see MOF82). It may be speculated, therefore, that their

observed suppressions of the martensitic transformation were the result of hydrogen contamination.

Interstitials may also result in an alteration of the martensitic structure. Hammond (HAM72) has suggested that the factors (i.e. interstitials) which give rise to a tetragonal distortion of the martensite in steels may also cause an orthorhombic distortion of the martensite in titanium alloys. While Hammond believes that carbon was the important impurity in both cases, it has been shown (MOF82) that hydrogen in Ti-Nb alloys causes a significantly expansion of the  $\beta$ phase lattice, ultimately leading to a tetragonal distortion of the BCC structure. Thus, all interstitials must be considered when examining this possibility. In addition, it may be possible for an  $a^{-}$ + distorted  $\beta$  structure to be misinterpreted as an orthorhombic structure.

3.3 The @ Phase

The  $\omega$  phase is a high pressure phase of pure titanium and zirconium. The P-T diagram of titanium is shown in Figure 3.5 (BUN65). An extrapolation of the  $\beta/\omega$  boundary shows that at atmospheric pressure (.1MPa), metastable  $\omega$ -Ti would transform to  $\beta$ -Ti at ~470C. In practice, however, it was found that  $\omega$ -Ti reverted to  $\alpha$ -Ti between 200 and 300C (BUN65). This fact, and other calculations have lead Vohra (VOH78) to suggest that the  $\alpha/\omega$  boundary in pure titanium may be susceptible to considerable hysteresis.



FIGURE 3.5 The pressure-temperature phase diagram of pure titanium (from BUN65)

Precipitates of the  $\omega$  phase have been observed in alloys of titanium and zirconium with several other transition elements. Precipitation has been found to occur during both quenching and isothermal aging. The  $\omega$  phase also can be formed in Ti-Nb alloys upon application of hydrostatic pressure (AF073). In Ti-Nb alloys,  $\omega$ precipitates have been observed in alloys with less than ~30% Nb.

## 3.3.1 Mechanics of Formation of the w Phase

There have been several studies as to how the  $\omega$  phase forms (COO69, DEF70, DEF71). It was shown (DEF70) that for a particular set of interatomic force constants, a BCC structure is unstable with respect to a transverse 1/3(112) phonon. This phonon is crystallographically equivalent to a longitudinal 2/3<111> phonon. The effect of these phonons can be visualized with the help of Figures The 2/3(111) phonon leaves every third  $(111)\beta$  plane 3.6a and b. unshifted, but collapses the middle two together. The atomic shifts are in the <111> direction and are only  $\sqrt{3}$  a/12 in length, i.e. less than .05nm. Chang, et al. (CHA76), on the basis of high resolution TEM, demonstrated that this process leads to the existence of three  $\omega$ subvariants. These are shown schematically in Figure 3.6c.

In a later paper (DEF71), it was postulated that the  $\beta \neq \omega$  transformation required a thermally activated nucleation process. If such were not the case, a total transformation of the BCC lattice to the  $\omega$  structure would occur. It was proposed that the  $\beta \neq \omega$ 



.

FIGURE 3.6 Schematics of the mechanism of  $\omega$  phase formation a) 2/3<111> phonon and its effect on the (111) $\beta$  planes b) Resultant  $\omega$  phase precipitate

÷,



FIGURE 3.6c Schematic of the three  $\boldsymbol{\omega}$  sub-variants

۰.

.

transformation would take place in a localized region of the crystal when the amplitude of a 2/3<111> phonon was large enough to overcome the free energy barrier between the two states.

The size and internal structure of an  $\omega$  region depend on temperature (DEF71). At high temperatures, the  $\omega$  structure would not be able to form from the  $\beta$  matrix. With decreasing temperature, phonon energy and coupling decrease, allowing a partial collapse of the (111) $\beta$  planes and the formation of  $\omega$  regions with a broad  $\beta/\omega$ The various 2/3<111> phonons act independently at low interface. temperatures, permitting the complete collapse of the (111)ß planes and the formation of  $\omega$  precipitates with sharp interfaces. This  $\beta \neq \omega$ transformation mechanism is reversible with temperature, provided that atomic diffusion does not alter the local composition, "locking-in" The reversible nature of this mechanism was the w structure. demonstrated by cooling a Ti - 8% Mo specimen in an electron microscope and observing the changes in the electron diffraction patterns (DEF71).

3.3.2 Crystal Structure and Orientation Relationships

The structure of the  $\omega$  phase is hexagonal with a space group of P6/mmm (SIL58, SIL70, HIC69). The atomic positions in this structure are: (0, 0, 0), (2/3, 1/3, 1/2), and (1/3, 2/3, 1/2).

As noted in the previous section, the  $\omega$  phase is formed by a slight distortion of the  $\beta$  phase. The orientation relationships,

which follow directly from the atomic displacements, are (SIL58):

<0001> ω || <111> β

As there are 4 <111> directions in the BCC structure, there are 4 variants of  $\omega$  precipitates. For each variant, there are 3 equivalent sub-variants (CHA76).

The lattice parameters of the  $\omega$  phase also follow from the atomic displacements. The theoretical lattice parameters are:  $a_{\omega} = \sqrt{2} a_{\beta}$ ,  $c_{\omega} = \sqrt{3} a_{\beta}/2$ , c/a = .6124. For these lattice parameters, the atomic volumes of the  $\omega$  and  $\beta$  structures are identical. Using XRD techniques, Hickman (HIC69a) measured the  $\omega$  lattice parameters in a Ti-Nb alloy and found: a =.4627nm, c =.2836nm, c/a = .6129.

# 3.3.3 Athermal $\omega$

Very fine, "diffuse"  $\omega$  precipitates have been found in several Ti-Nb alloys after quenching from high temperatures. These precipitates, which cannot be observed by bright field TEM, are generally detected in electron diffraction patterns. The  $\omega$  phase reflections in these patterns can be used to form dark field images of the precipitates. The precipitates form as ellipsoids of revolution and range in size from 1 to 6nm in length, but are typically about 2nm long.

The precipitation of  $\omega$  on quenching depends greatly on the quench rate/temperature and alloy composition. It has been demonstrated

(HAT68, MOR73) that in those alloys where  $\alpha$ " may form, a fast quench will produce  $\alpha$ ", while a slow quench will produce  $\omega$  precipitates. Unfortunately, few studies have reported actual quench rates, giving instead the type of quench and the initial temperature. A summary of quench temperatures and alloy compositions for which athermal  $\omega$  phase precipitation has been observed is shown in Figure 3.7.

A confusing result of the study of Balcerzak and Sass (BAL72) was that, for a given alloy, increasing the quench temperature promoted the precipitation of  $\omega$  over the formation of  $\alpha$ ". This result, which was not understood by the original authors, is puzzling in that one would have expected the quench rate to have been faster the higher the quench temperature. On the other hand, the higher the quench temperature, the longer would have been the actual duration of the quench. This may have allowed sufficient time for the atomic shuffles which produce the  $\omega$  structure to have taken place.

Another interesting result of the work of Balcerzak and Sass (BAL72) was the observation of rows of  $\omega$  precipitates in the <lll> $\beta$  directions. These appeared to coalesce on aging to form first "rafts" of precipitates, then larger precipitates. This row morphology has been observed in other alloy systems as well (SAS69, SAS72, DYA83).

The composition of athermal  $\omega$  precipitates long has been assumed to be the same as that of the matrix (HIC69). This is reasonable in that during the quench there is insufficient time for any long range diffusion to occur. Good supporting evidence for this assumption was given by Lyon (LY081). Electron microscopy indicated extensive  $\omega$


FIGURE 3.7 Microstructures produced during quenching from the indicated temperatures (from KRA67, HAT68, BAK69, VOZ70, BAL72, MOR73, LYO81)  $\Delta - \beta + \omega, \quad \nabla - \beta + \alpha'', \quad \diamondsuit - \beta$ 

phase precipitation in a quenched 21.7% Nb alloy. Small angle x-ray scattering (SAXS), however, indicated that the specimen was single-phase. As SAXS is sensitive only to differences in electron density, it was concluded that the precipitates and matrix must have been of the same composition.

The effect of cooling below room temperature was the subject of two investigations of quenched Ti-V and Ti-Mo alloys (DEF71, DYA83). It was found, using TEM and XRD, that the  $\omega$  diffraction spots at room temperature were diffuse, indicating that the collapse of the  $(111)\beta$ planes to form the  $\omega$  structure was incomplete. The  $\omega$  spots became sharper and more intense on cooling below room temperature. D'yakonova, et al. (DYA83) found that the spot intensities increased more than was calculated from the Debye-Waller effect. This increase, however, was compensated by a decrease in the dimensions of the diffraction spots in such a way that the total integrated intensity varied according to the Debye-Waller effect. These results implied that cooling did not cause the formation of additional  $\omega$  phase precipitates, but, rather, caused a refinement (i.e. a more complete collapse of the (111)ß planes) of the crystal structure of the existing  $\omega$  precipitates. (It is not clear, however, that this was the original interpretation.) The diffraction effects were found to be reversible with temperature. These results confirm the theory of the mechanics of  $\omega$  phase formation of deFontaine, et al. (DEF71).

#### 3.3.4 Isothermal $\omega$

It is implicitly understood in all studies of the isothermal formation and growth of  $\omega$  phase precipitates that the specimens examined had been quenched from the high temperature, single-phase region to room temperature first, and then aged at an elevated temperature. There has been only one report (FR080, investigating a commercial Ti-Mo-Zr-Sn alloy) of the isothermal formation of  $\omega$  phase precipitates without an intervening room temperature quench. Because of this, the effect of heating on the original, as-quenched microstructure must be considered when discussing the isothermal  $\omega$ phase.

The original, as-quenched microstructures may consist of either  $\beta$ ,  $\beta + \alpha''$  or  $\beta + \omega$ , depending upon alloy composition and quench rate. The short term effect of heating on the  $\beta$  and  $\beta + \omega$  structures has not been studied in detail. It was noted in passing (LY083), however, that resistance measurements indicated that a 21.7% Nb alloy -- which initially had a  $\beta + \omega$  structure -- reverted to  $\beta$  at 200 - 300C during reheating and then reformed a  $\beta + \omega$  structure isothermally at 300 -450C.

The decomposition of the  $\beta$  +  $\alpha$ " structure has been reported to follow two different paths (HAT68, BAK69, HIC69a, FL082). The first two studies, using LM, XRD and TEM, reported that in ~21% Nb alloys complete reversion of  $\alpha$ " to  $\beta$  occurred within 2 - 4 minutes at 330C and that precipitation of the  $\omega$  phase began after ~5 minutes. Hickman

(HIC69a) found that  $\alpha$ " reverted to  $\beta$  followed by the immediate precipitation of  $\omega$  during aging above 200C for a 22% Nb alloy, 150C for a 25% Nb alloy,.

Flower, et al. (FLO82) have interpreted TEM micrographs to indicate that  $\alpha$ " in Ti-Nb (and Ti-V and Ti-Mo) alloys undergoes a spinodal decomposition. This mode of decomposition was observed in quenched alloys as well as in a 7.7% Nb alloy heat treated 100 minutes at 525C and an 11.4% Nb alloy heat treated at 375C. Above these temperatures it was found that  $\alpha$ " reverted to  $\beta$ . Because the interdiffusion coefficient increases exponentially with decreasing niobium content (see section 4.2.4), it is difficult to correlate the results of Flower, et al. with those cited above. On the basis of related investigations (DAV79, DAV79a), it may be assumed that the TEM specimens of Flower, et al. were electropolished. Microstructures similar to those observed by Flower, et al. were observed during the course of the present study and were concluded to be electropolishing artifacts. For these reasons, the interpretations of Flower, et al. are subject to some doubt.

At the aging temperature,  $\omega$  phase precipitates form and grow. The temperatures and compositions at which isothermal  $\omega$  phase precipitation has been observed are summarized in Figure 3.8. As for the athermal form, the precipitate morphology is that of an ellipsoid of revolution with the ratio of the major to minor axes generally being 2.5 - 3 (KRA67, BAK69, VOZ70, LY081), though ratios as high as 5 have been reported (KRA67, BAK69). A rod-like morphology has been



FIGURE 3.8 Microstructures produced during isothermal aging at the indicated temperatures (from KRA67, HAT68, BAK69, HIC69a, VOZ70, BAL72)  $\Delta - \beta + \omega$ ,  $\nabla - \beta + \alpha$ 

reported in a commercial Ti-Mo-Zr-Sn-O alloy (FAT83) in which the ratio of the axes was ~10.

The kinetics of the growth of isothermal  $\omega$  were the subject of two studies (MOR73, LYO81). Studying a 16.7% Nb alloy Morniroli and Gantois (MOR73) found that the size distribution of the precipitates was narrow for aging times up to 2 hours. This broadened considerably with increasing time. For times up to 120 hours at 400C, it was found that the major axis of the precipitates lengthened as t<sup>1/3</sup>. An activation energy of ~21 kcal/mole was derived from measurments of the precipitate growth as a function of temperature for 2 hour heat treatments between 391 and 453C. Using their tabulated data, however, an activation energy of only 16.7 kcal/mole was calculated in the course of this review.

Lyon (LYO81) used both TEM and SAXS in his investigation of the  $\omega$  phase growth kinetics in a 21.7% Nb alloy. The specimens initially consisted of  $\beta + \omega$ . The precipitate size distributions were found to vary in the same manner as noted above (MOR73). On the basis of TEM measurements, the major axis of the precipitates was found to increase as  $t^{1/5}$  for times up to 232 hours for temperatures between 378 and 438C. SAXS measurements of the length of the major axis always yielded values about 1.6 times smaller than those measured using TEM. In addition, the SAXS measurements of the precipitate dimensions showed little time dependence for aging times longer than 25 hours. These results are in marked contrast to that of Morniroli and Gantois (MOR73). The SAXS intensity curves also indicated that the  $\omega$ 

precipitates did not have a uniform electron density. The differences in the TEM and SAXS results were reconciled by proposing that the  $\omega$ precipitates were poor in Nb, but were surrounded by Nb-rich shells. (This shell/precipitate structure has been proposed by others (HAT68, BAK69) as well.) The uncertainties in the interpretations of the SAXS measurements, however, leave the appropriateness of this proposal in some doubt.

The discrepancies in the growth kinetics between these two studies are yet to be resolved. The answer may lie in the different compositions of the two alloys, or in differences in the initial state, vacancy supersaturation, or interstitial content of the two alloys.

The composition of the isothermal form of the  $\omega$  phase was investigated by Hickman (HIC69a) using the XRD technique of Bond (BON60). The change in lattice parameter of the matrix was measured as a function of heat treatment time and temperature in order to determine the composition of the matrix. The intensities of the  $\beta$  and  $\omega$  reflections were measured and used to calculate the volume fraction of  $\omega$  precipitates. These data were combined to calculate the composition of the  $\omega$  phase precipitates. It was concluded that the terminal  $\omega$  composition was about 9% Nb.

The results of this study are subject to some doubt for the following reasons. The method of determining the  $\omega$  phase volume fraction was not clear, though it is quite important to the compositional calculations. At short aging times it was found that

the ß phase lattice parameter contracted instead of expanded. This was attributed to elastic effects, which seems doubtful in that the atomic volumes of titanium and niobium differ by less than 2% (BAR66). The atomic volume differences of the constituents of the other alloys investigated (Ti-Mo, Ti-Fe, Ti-Cr) are much larger, yet similar effects were not noted. The error in the lattice parameter measurements was stated as being +.02pm (the Bond technique can be precise to +.001pm (BON60)). Shifts of only .06 to .1pm were reported in alloys of 22 and 25% Nb. In alloys of these compositions, the variation of the BCC lattice parameter with composition is only about .01pm/at%, Nb (see section 4.5.2). The results of section 4.5.2 also show that variations in the lattice parameter of the magnitude measured by Hickman may be due to variations in the preparation of XRD All of these combine to make an estimate of matrix specimens. composition based on the  $\beta$  phase lattice parameter very difficult.

### 3.3.5 Effects of Interstitials

There have been several studies of  $\omega$  phase formation as a function of interstitial content. Unfortunately, only one was concerned specifically with the Ti-Nb system (HAN85) -- the rest investigated either the Ti-V or Ti-Mo systems. In addition, most of the studies used indirect methods to examine the effects of interstitials -- only four used TEM or XRD (PAT73, FR080, HAN85, HAY85).

The effects of oxygen are fairly well established. Examining a 22.5% Nb and a 22.5% Nb + 1.3% O alloy with TEM, Hanada, et al. (HAN85) found that oxygen suppressed the formation of athermal  $\omega$  and retarded the growth kinetics of isothermal  $\omega$ . At the same time, precipitation of  $\alpha$  was enhanced. The same effects were observed by Froes, et al. (FRO8O) in a Ti-Mo-Zr-Sn alloy. Paton and Williams (PAT73) found that oxygen additions lowered the  $\omega$  start temperature in several Ti-V alloys. In a 19% V alloy, the  $\omega$  start temperature was lowered from OC for an oxygen content of .076%,0, to -165C for .227% O.

It is interesting to note that  $\delta$ -titanium oxide has the same crystal structure as the  $\omega$  phase. The composition of this oxide has been estimated to be Ti<sub>2</sub>O and its lattice parameters are: a = .499nm, c = .288nm, c/a = .5767 (AND59).

There are conflicting interpretations as to the effect of hydrogen additions on  $\omega$  phase formation. Using XRD techniques, Hayman and Gerberich (HAY85) found that up to 9.8% H in an 8.7% Mo alloy had no effect on the formation of athermal  $\omega$ , although both the  $\beta$  and  $\omega$ lattices were expanded. In an 11.1% Mo alloy, however, they found that 12.9% H suppressed athermal  $\omega$  formation. In contrast to this study, the data of several investigations based on measurements of internal friction and the elastic moduli in Ti-V and Ti-Mo alloys have been interpreted as indicating that hydrogen additions promote the  $\beta \neq \omega$  transformation (AHL78, PAT75, PAT76). Guiles and Ono (GUI76), however, using the same techniques, were more cautious in their

analysis and effectively discounted the previous claims. As this debate is centered on the analyses of internal friction measurements in alloy systems not of immediate interest, no conclusions about the effect of interstitial hydrogen on the formation of the  $\omega$  phase in Ti-Nb alloys can be drawn.

3.4 Related Phenomena

Measurements of resistivity and microhardness are often used to follow the course of a precipitation reaction. In addition, they provide valuable information to the engineering and physics community. These techniques, though, provide only indirect measures of a particular reaction — they cannot, of themselves, identify the nature of a reaction.

There have been several investigations which have included measurements of resistivity and hardness. As noted in sections 3.2 and 3.3, the microstructures of the high titanium alloys are very sensitive to thermal history and to interstitial impurities. Most of the studies to be discussed in this section gave insufficient details of their sample preparation techniques offered and scant microstructural information, making interpretation of their results difficult. Consequently, the resistivity and hardness data will be given at this point for completeness and future reference, but a detailed analysis will not be offered until the discussion of the results of the present study.

#### 3.4.1 Resistivity Measurements

Measurements of the resistivity,  $\rho$ , of alloys of titanium with other transition metals have shown two anomalies (COL84). The compositional dependence of the isothermal resistivity does not exhibit the expected solid solution behavior. Also, the resistivities several high titanium alloys show a negative temperature of i.e. they become more resistive with decreasing dependence, temperature. For a summary of results pertaining to related alloy systems, see the review of Collings (COL84).

The composition dependence of  $\rho$  for Ti-Nb alloys is shown in Figures 3.9a and b. The data in Figure 3.9a are for 273 and 77K (73K for AME54), those in Figure 3.9b for T<sub>c</sub> (1.2K in a magnetic field for BER63). All of the specimens used in these investigations had been annealed and quenched, with the exception that some of those of Berlincourt and Hake (BER63) had been cold-worked.

The temperature coefficient of resistivity,  $\partial \rho / \partial T$ , between 273 and 77K is shown as a function of composition in Figure 3.10. The data of both Ames and McQuillan (AME54) and Prekul, et al. (PRE75) showed slight positive deviations from linearity between 273K and 77K. The latter set of data also showed that below about 40K,  $\partial \rho / \partial T$ approached 0. The data of Prekul, et al. and Hochstuhl and Obst (HOC82) showed that for those alloys with a negative  $\partial \rho / \partial T$ , the resistivity reached a maximum around 80K, below which temperature  $\partial \rho / \partial T$  was positive.



FIGURE 3.9a Resistivities of Ti-Nb alloys (from the literature) Open symbols: room temperature resistivities Closed symbols: 77K resistivities



FIGURE 3.9b Resistivities at  $T_c$  (from the literature)



FIGURE 3.10 Temperature coefficient of the resistivity between room temperature and 77K (from the literature)

These studies did offer some microstructural and processing information about their specimens. LM of the 20% Nb specimen used by Ames and McQuillan showed retained  $\beta$ . The 10, 20 and 25% Nb specimens of Berlincourt and Hake were found not to be single phase (using XRD), but the phases present, other than  $\beta$ , were not determined. All but the 25% Nb specimen of Prekul, et al. were water quenched from 1100C. Hochstuhl and Obst assumed that their specimen was single phase  $\beta$ .

Sections 3.2 and 3.3 showed that alloys whose compositions are between 18 and 30% Nb form either  $\beta + \alpha''$  or  $\beta + \omega$  on quenching. This is just the range of compositions in which a negative  $\partial \rho / \partial T$  has been observed. Since only extremely fast quench rates may produce single phase  $\beta$  specimens (JEP70), it may be concluded that those specimens assumed to be single phase (AME54, HOC82), as well as the 25% Nb alloy of Prekul, et al., in fact consisted of  $\beta + \omega$ .

The anomalous composition dependence of  $\rho$  has been discussed in the literature (COL74, LAR80), but has not received intensive experimental study. Collings (COL74) suggested that it is due to a combination of irreversible  $\omega$  phase precipitation and soft phonons, the latter being the source of anomalous resistivity in solute rich alloys. Larbalestier (LAR80) attributed this anomaly to an increasing phonon amplitude caused by a decreasing shear modulus as the  $\beta$  transus is approached.

There has been much discussion in the literature as to the cause of the anomalous temperature dependence of the resistivities of titanium-based alloys. It has been attributed either to the reversible formation of athermal  $\omega$  precipitates (H072, COL74, COL78), to the refinement of the crystal structure of existing  $\omega$  precipitates (DYA83), or to the BCC lattice instability which causes the precipitation (CHA74, COL74).

D'yakonova, et al. (DYA83) used TEM to study the effects of cooling on a series of quenched Ti-V alloys. On the basis of SAD measurements, it was determined that cooling these alloys resulted in a more complete collapse of the (111) $\beta$  planes in the as-quenched  $\omega$ precipitates, rather than in an increase in the amount of  $\omega$  phase precipitation (see section 3.3.1). Intensities of the  $\omega$  phase reflections were measured at room temperature and at -160C (or -180C) and their ratios determined. In the 19 and 23% V alloys, the measured intensity ratios were 4 to 5 times the calculated values, and  $\partial \rho/\partial T$ was found to be negative. In the other alloys (13, 17 and 40% V),  $\partial \rho/\partial T$  was positive and the increase in the intensity ratios was only 20 to 60% above the calculated values.

Studying a series of Ti-Cr alloys, Chandrasekaran, et al. (CHA74) concluded that a negative  $\partial \rho / \partial T$  was due to the instability, per se, of the BCC lattice with respect to the  $\omega$  structure. Two alloys which exhibited a negative  $\partial \rho / \partial T$  were examined in an electron microscope using a cold stage capable of attaining ~93K. Neither showed evidence in SAD of the formation of  $\omega$  precipitates. From this it was concluded that a negative  $\partial \rho / \partial T$  was a property of the metastable BCC lattice itself and was not due to the reversible formation of athermal  $\omega$  phase precipitates. In addition, it was noted that the same alloys after

isothermal aging, which did produce  $\omega$  precipitates, possesed a positive value of  $\partial \rho/\partial T$ .

Hochstuhl and Obst (HOC82) proposed the same mechanism for a 22% Nb alloy; however, they postulated that at about 80K (the temperature of maximum resistivity in their alloy),  $\omega$  precipitates formed, allowing the lattice to relax and exhibit a positive  $\partial \rho / \partial T$  with further cooling. Their curve of  $\rho$  vs T was found to be reversible with the exception that plastic deformation at 180K caused  $\rho$ o to drop significantly and  $\partial \rho / \partial T$  to be always positive.

#### 3.4.2 Vicker's Hardness Measurements

The results of hardness measurements on annealed and quenched alloys are shown in Figure 3.11. The data of Guzei (GUZ66), Guseva (GUS82) and Collings (COL84) are in fairly good agreement. (The data of GUS82 were obtained from alloys which had been quenched from 1000C.) These data show a sharp maximum at approximately 13.5% Nb. The data of Bagariatskii, et al. (BAG59) exhibit the same compositional dependence, though at significantly greater hardness values.

Some microstructural information was given in these studies as well. The upper limit of martensite formation was determined to be ~12% Nb (GUZ66 using LM) or ~14.5% Nb (BAG59 using XRD). XRD also indicated that the 12 to 20% Nb alloys of GUS82 contained  $\beta + \alpha'' + \omega$ . Precipitation of the  $\omega$  phase was found to be responsible for the peak



FIGURE 3.11 Vicker's hardness numbers (from the literature)

in the hardness curve (BAG59, GUS82). Alloys containing more than 20% Nb were found to be single phase  $\beta$ .

3.5 Results of the Present Investigation - Quenched Alloys

The effect of quench rate on microstructure was investigated in this part of the present study. The alloys were quenched to room temperature after recrystallization at 1000C. The measurement of the quench rates produced in this study was discussed in section 2.3.1. These quench rates are shown again in Figure 3.12.

The microstructures produced during quenching were found to be in general agreement with the data of the literature. Not reported in the literature, however, were the significant effects these microstructures had on the resistivities and hardnesses of these alloys.

## 3.5.1 Microstructures Resulting from the Fast Water Quench

The FW quench produced a martensitic structure in the 20 and 25-FW specimens. An SAD pattern and bright field micrograph from the 20-FW specimen are shown in Figures 3.13a and b. The  $\beta + \alpha$ " diffraction pattern is very similar to the  $\beta + \alpha$  pattern (see Appendix A). The  $\alpha$ " orientation relationships given in section 3.2.1 are confirmed in this diffraction pattern. The bright field image shows a strained and heavily faulted microstructure. Large regions of single



FIGURE 3.12 Quench rates produced in the present study (measured using the specimen shown in Figure 2.2)



FIGURE 3.13 TEM micrographs of the 20-FW specimen
a) [110] SAD pattern showing β and α" reflections
b) Bright field image

phase  $\beta$  were quite common in the 20-FW TEM specimen. These  $\beta$  regions showed no evidence of  $\omega$  phase precipitation, though there was some very slight reciprocal lattice streaking in the  $\omega$  positions.

Light metallography indicated that the 25-FW specimen had substantially, but not completely, transformed to martensite. This was evident in the center of the specimen where very fine  $\omega$  phase precipitates in a  $\beta$  matrix were found using TEM.

The 30 and 35-FW specimens were found to be single phase  $\beta$ . SAD patterns from these specimens, however, showed some reciprocal lattice streaking (examples of this streaking will be given in section 3.5.2). This streaking, which is the result of the BCC structural instability, indicated that the transformation of the matrix to the  $\omega$  structure was in its very early stages, but had not produced actual precipitates. This condition will be referred to hereafter as the formation of "virtual"  $\omega$  precipitates.

The 30-FW LM specimen was submerged in liquid nitrogen in an attempt to produce a martensitic structure. No rumpling of the specimen surface was observed after warming the specimen to room temperature.

X-ray diffraction studies of the 20-FW specimen were complicated by the metastable nature of the microstructure. It was found that powders of this specimen did not retain the martensitic microstructure through the filing and annealing processes. In order to obtain some information about the martensite, a solid specimen was used. A short length of 3mm rod was cut from the 20% Nb alloy, annealed at 1000C and FW quenched, and then round-rolled until it was ~.5mm in diameter. This wire was sealed in a quartz tube, as described in section 2.3, and annealed for 2 hours at 1000C.

The FW quench was difficult to reproduce in the wire specimen. It was undesirable to quench such a small specimen directly into water because of contamination considerations. It was found, however, that a residual argon atmosphere of 100 Torr, coupled with quenching the tube, without breaking it, into liquid nitrogen produced a martensitic specimen.

The d-spacings determined for the 20-FW wire specimen are given in Table 3.2. Due to the relative bulk of the specimen, absorption of the Cu Ka x-rays caused the low angle diffraction lines to be shifted significantly. The orthorhombic lattice parameters were not calculated, though the diffraction pattern could be indexed as  $\beta + \alpha''$ .

3.5.2 Microstructures Resulting from the Air Cool Quench

The AC quench allowed the formation of  $\omega$  phase precipitates in many of the AC specimens. The presence of  $\omega$  precipitates could be detected easily in SAD patterns. SAD patterns from the AC specimen series are shown in Figures 3.14a - h. For an analysis of these electron diffraction patterns, see Appendix A.

The  $\omega$  diffraction spots gradually become less sharp as the niobium content of an alloy is increased. Using these spots, the  $\omega$  precipitates could be imaged in dark field in the 20 and 25-AC

# TABLE 3.2

.

٠

d-spacings of the 20-FW Wire Specimen

<u>d (nm)</u>	HKL (α")	<u>ΗΚL (β)</u>
.26287	110	
.25247		
.23693	020	
.22868	111	110
•21114	021	
.16539	022	
.16317		200
.15829	200	
.14222	130	
.13576	131	
.13312	113	211
.13061	202	
.12710	221	
.12125	132	
.11559	004	220
.11478	222	
.10357	310	310
.09554	043	
.09458		222
.09366	204	
•08764 <sup>'</sup>		321
.07737		330



FIGURE 3.14 [110] SAD patterns of the AC specimens showing the change in w phase precipitation from "real" to "virtual" a) 20-AC, b) 25-AC, c) 30-AC, d) 35-AC



FIGURE 3.14 [110] SAD patterns of the AC specimens showing the change in w phase precipitation from "real" to "virtual" e) 40-AC, f) 50-AC, g) 60-AC, h) 70-AC

specimens. As a consequence, these precipitates were classified as "real". The intensities of the  $\omega$  reflections in the SAD pattern of the 30-AC specimen were insufficient to produce a dark field image, though they are sharper and more intense than those of the 30-FW specimen. The other specimens appear to be single phase  $\beta$ , though considerable reciprocal lattice streaking can be observed in specimens with compositions of up to 50% Nb. As in the 30 and 35-FW specimens, this streaking indicates the presence of "virtual"  $\omega$  precipitates. (It should be noted that in order to show this streaking, these SAD patterns received ~10 times the exposure of other diffraction patterns.)

Representative of the microstructures of the 20, 25 and 30-AC specimens are those shown in Figures 3.15a, b and c. Figure 3.15a is a dark field micrograph of the 20-AC specimen showing dense precipitation of very small  $\omega$  precipitates. It should be remembered that these precipitates represent only 1/4 of the total  $\omega$  phase precipitation.

The bright field micrographs in Figures 3.15b and c show a very different type of precipitate. Extensive tilting of the specimen did not produce any additional reflections in SAD, nor did it cause the appearance of these precipitates to change appreciably. The precipitates are visible in bright field due to the large strain fields surrounding each. These strains indicate that the precipitates are at least semi-coherent with the matrix.



The 20-AC LM specimen showed a densely precipitated structure, but it was beyond the resolving power of LM. There appeared to be transformation free zones at the grain boundaries. The rest of the LM specimens appeared to be single phase.

Polished specimens of the 20 and 25-AC alloys were submerged in liquid nitrogen in an attempt to produce a martensitic structure. Again, no surface rumpling was observed after warming the specimens to room temperature.

The x-ray diffraction pattern of a 20-AC wire specimen was confusing. The diffraction pattern indicated a two phase structure, but the second phase could not be indexed as  $\omega$ . The d-spacings determined for this specimen are given in Table 3.3.

#### 3.5.3 Microstructures Resulting from the Furnace Cool Quench

The general microstructural features of the AC specimen series were reproduced in the FC specimen series. The slower cooling resulted in sharper and more intense  $\omega$  phase reflections in the SAD patterns of the specimens. This was particularly noticable in the 35% Nb specimen. The FC quench also allowed for growth of the  $\omega$ precipitates during the quench. This can be seen in the micrographs of Figures 3.16a and b. These are dark field micrographs of the 20-AC and 20-FC specimens. It can be seen that the  $\omega$  precipitates in the FC specimen are larger and have greater definition than those in the AC specimen.

# TABLE 3.3

d-spacings of the 20-AC Wire Specimen

<u>d (nm)</u>	<u>ΗΚL (β)</u>
.28086	
.25378	
.22972	110
.21902	
.21026	
<b>.</b> 20494	
.16334	200
.15061	
.14604	
.14202	
.14013	
.13623	
.13353	211
.11576	220
.10369	310
.09467	222
.08/70	321
.08/69	321
.08208	400
.08206	400
.07739	330
.07739	330



FIGURE 3.16 Comparison of ω phase precipitation as a function of quench rate (Dark field images) a) 20-AC, b)20-FC

Precipitates of the type shown in Figures 3.15b and c were not found in the 20-FC TEM specimen. They were observed, however, in the 25 and 35-FC TEM specimens.

3.5.4 Resistivities of the Quenched Alloys

The isothermal resistivities as a function of composition for the FW and AC specimens are shown in Figures 3.17a, b and c for room temperature (~295K), 77.4K and  $T_c$  (~10K), respectively. (All of the alloys in this study became superconducting in liquid helium, so the resistivities reported for  $T_c$  are actually the normal state resistivities just above the superconducting transition temperature,  $T_c$ .) The data are presented in Table 3.4. These resistivity values were found to be reproducible with temperature cycling.

Several results are demonstrated in Figures 3.17. There is no indication of conventional solid solution behavior ---the resistivities show a continued increase with decreasing niobium content. For alloys with compositions of 30% Nb or more, the resistivities are not significantly affected by quench rate. The resistivities of the 20 and 25-AC specimens are greater than those of 20 and 25-FW specimens at all temperatures. the Below room temperature, the resistivities of the 20 and 25-FW specimens drop significantly while those of the 20 and 25-AC specimens remain high. This marked effect due to quench rate has not been reported in the literature.



FIGURE 3.17a Resistivities at room temperature of the FW and AC specimens (data given in Table 3.4)



FIGURE 3.17b Resistivities at 77K of the FW and AC specimens (data given in Table 3.4)



FIGURE 3.17c Resistivities at  $T_{\rm C}$  of the FW and AC specimens (data given in Table 3.4)

# TABLE 3.4

#### Resistivities of the Quenched Alloys

	FW				AC		FC		
<u>% Nb</u>	295	77.4	Tc	295	77.4	Tc	295	77.4	T <sub>c</sub>
20 25 30 35 40 50 60	99.2 91.3 82.0 75.2 68.9 60.9 53.1	78.2 85.6 78.9 67.8 60.8 50.2 41.9	70.8 82.2 77.3 65.4 58.0 47.1 38.8	106.0 93.9 81.7 75.5 69.0 60.6 52.4	106.4 96.6 79.1 68.7 60.2 50.0 41.5	105.6 95.8 77.8 66.7 57.8 47.1 38.5	104.4 94.4 82.9 75.1 69.2 60.5 52.2	103.1 96.2 80.7 68.7 60.4 50.0 41.2	101.7 95.7 79.3 66.7 57.9 46.9 38.1
70 100	44.6 14.5	33.2 2.54	30.1 .164	44.4	33.0	30.0	43.8	32.6	29.6

# Resistivities in $\mu\Omega-\text{cm}$ Temperatures in Kelvin Alloys quenched from 1000C to room temperature

## TABLE 3.5

Temperature Coefficients of the Resistivities

	I	FW			С	FC	FC		
% Nb	ρο	<u>96</u> 3Τ		ρο	<u>96</u> 76	ρο	<u>η6</u> Τ6		
20 20	70.38	.0977		106.54 105.52	0018+ .0114*	101.97	.0087		
25 25	82.54	.0303		97.51 95.76	0123+ .0103*	96.9 95.59	0086+ .0083*		
30	77.36	.0161		77.85	.0131	79.45	.0121		
35	65.18	.0337		66.33	.0309	66.44	.0295		
40	57.75	.0378		57.26	.0394	57.43	.0399		
50	46.53	.0487		46.53	.0470	46.38	.0478		
60	38.15	.0507		37.85	.0488	37.50	.0498		
70	29.45	.0510		29.33	.0503	28.94	.0504		
100	786	.0512							

Po in  $\mu\Omega$ -cm,  $\partial\rho/\partial T$  in  $\mu\Omega$ -cm/K Temp Range: 295K - T<sub>c</sub>; except +(295K - 77K), \*(77K - T<sub>c</sub>) Alloys quenched from 1000C to room temperature
When plotted as a function of temperature, the data for each quench series formed a series of straight lines of the form:

$$\rho = \rho_0 + T * \partial \rho / \partial T$$

Continuous measurements of  $\rho$  as a function of T were not made, making it impossible to determine if there were any actual deviations from linearity. Exceptions to this were the 20-AC, 25-AC, and 25-FC specimens which exhibited a negative  $\partial \rho / \partial T$  between 295 and 77K. In all specimens, regardless of quench rate,  $\partial \rho / \partial T$  was positive between 77K and T<sub>c</sub>. The data for  $\rho o$  and  $\partial \rho / \partial T$  are presented in Table 3.5, and are plotted in Figures 3.18a and b, respectively. The temperature range for these data is 295K to T<sub>c</sub>, except as noted.

#### 3.5.5 Vicker's Hardness Numbers of the Quenched Alloys

The compositional dependence of the Vicker's hardness number, VHN, as a function of quench rate is shown in Figure 3.19. Also plotted are the hardness values of the swaged alloy rods before the de-hydrogen anneal (these rods had been subjected to a true strain of approximately 2). The data are presented in Table 3.6. It is interesting to note that the VHN of the 40 - 100-FW specimens demonstrate a compositional dependence resembling that of conventional solid solution behavior.

The effect of the different microstructures produced by the different quench rates is quite apparent in these data. The FW specimens are quite soft when compared with the AC and as-swaged



FIGURE 3.18a Po for the FW, AC and FC specimens Open symbols:  $295K - T_C$ Half-closed symbols: 295K - 77KClosed symbols:  $77K - T_C$ (data given in Table 3.5)



FIGURE 3.18b əp/aT for the FW, AC and FC specimens Open symbols: 295K - T<sub>c</sub> Half-closed symbols: 295K - 77K Closed symbols:  $77K - T_c$ (data given in Table 3.5)



FIGURE 3.19 Vicker's hardness numbers of the FW, AC and swaged specimens (data given in Table 3.6)

## TABLE 3.6

Vicker's Hardness Numbers of the Quenched Alloys

<u>% Nb</u>	Swaged*	FW	AC
0	225	145	
20	245	174	258
25	224	149	198
30	197	130	172
35	169	113	151
40	156	102	138
50	167	145	146
60	189	157	159
70	197	156	155
100	101	68	

100g load -- Typical Errors: 3% Alloys quenched from 1000C to room temperature \* True strain of ~2 specimens. This effect has not been reported in the literature. As noted in the previous sections, the quench rate did not affect the properties of the 50, 60 and 70% Nb alloys.

#### 3.5.6 Discussion of the Results

A summary of the microstuctures of the quenched alloys is given in Table 3.7. Presented in this table are the second phases found in the specimens as a function of alloy composition and quench rate (the matrix phase in all cases is  $\beta$ ). The results presented in sections 3.5.1 - 3.5.3 show that the sensitivity of the microstructure of an alloy to quench rate increases with decreasing niobium content.

The conditions under which martensite could be produced in the alloys of the present study were in general agreement with those established in the literature. An FW quench produced  $\alpha$ " in specimens of the 20 and 25% Nb alloys, though it appears that M<sub>s</sub> is close to room temperature for a 25% Nb alloy. Submerging the 30-FW LM specimen in liquid nitrogen did not produce any surface rumpling. This indicates that M<sub>s</sub> for a 30% Nb alloy is below 77K. Submerging the 20 and 25-AC LM specimens in liquid nitrogen also failed to produce artifacts of a martensitic transformation. In these specimens, the martensitic transformation had been inhibited by the presence of  $\omega$  precipitates.

Comparison of these results with those of the literature show that two points are in need of further discussion. Figure 3.4 showed

		•	•	•
Quench	20	25	30	35
FW AC FC	ດ.'' ພ ພ	α" + ω ω ω	virtual ω ω ω	virtual ω virtual ω ω
Quench	40	50	60	70
AC	virtual ω	virtual ω	-	-

Alloy compositions in at% Nb Alloys quenched from 1000C to room temperature

# TABLE 3.7

Second Phases in the Quenched Alloys

the type of transformation to be expected for a given quench rate, according to Jepson, et al. (JEP70). This figure is reproduced in Figure 3.20, with the FW and AC quench rates of the present study plotted for the 20 and 25% Nb alloys. According to this figure, both quenches should have produced a martensitic structure in the 20% Nb alloy. The FW quench in the 25% Nb alloy should have produced single phase  $\beta$ , the AC quench, martensite. These disagreements may be due to the fact that the phase transformations which occur in very thin and bulk specimens do not always correlate with each other.

The second point to be discussed is the  $\alpha$ " lattice parameter data of Morniroli and Gantois (MOR73). Data were given by these authors for alloys with compositions of 25, 26.6 and 28.2% Nb. The results of the present study are in agreement with the M<sub>s</sub> data of section 3.2.2 which show that M<sub>s</sub> for these three alloys is at, or below, room temperature. Morniroli and Gantois did not indicate that any of their diffraction experiments were performed below room temperature, leaving their lattice parameter data for these three alloys in doubt.

Identification of the precipitates shown in the bright field micrographs of Figures 3.15b and c was not possible using SAD. Due to their asymmetrical shape, it is unlikely that these precipitates are  $\beta$ . They may have been  $\alpha$  nuclei, but the possibility that they are the result of contamination introduced during TEM specimen preparation also cannot be ruled out.

Precipitation of the  $\omega$  phase could be produced in most of the alloys of the present study under the appropriate quench conditions.



FIGURE 3.20 Critical quench rates for Ti-Nb alloys (from JEP70) showing the FW and AC quenches of the present study

Exceptions were the 50, 60 and 70% Nb alloys. The results of sections 3.5.1 - 3.5.3 show that the lower the niobium content of an alloy and/or the slower the quench rate, the more "real" and better defined are the  $\omega$  precipitates.

The compositional dependence of  $\omega$  phase precipitation in the Ti-Nb system may be understood in the following manner. (This interpretation is similar to that of Collings (COL74) for the Ti-V system, and in accord with the theory of deFontaine, et al. (DEF71) for the temperature dependence of the internal structure of  $\omega$  phase precipitates.) Decreasing the niobium content of an alloy causes the BCC lattice to become increasingly unstable. Initially, the lattice responds to this instability with a partial collapse of the  $(111)\beta$ With further planes to form "virtual" @ phase precipitates. reductions in niobium content the collapse of the (111) planes becomes more complete, eventually producing "real" w precipitates. The effect of this refinement of the  $\omega$  crystal structure with decreasing niobium content is shown in the sequence of SAD patterns in Figure 3.14. (Similar sequences have been published for the Ti-Nb (BAL72) and Ti-V (MCC71) systems.)

The effect of quench rate on the formation of  $\omega$  phase precipitates demonstrates two points. First, it confirms that the  $\beta + \omega$  transformation is thermally activated as postulated by deFontaine, et al. (DEF71). Second, it shows that diffusion during a quench not only promotes a more complete collapse of the (111) $\beta$ 

planes, but also enables growth of the  $\omega$  precipitates. This latter point is demonstrated in Figures 3.16.

A subtle result of this study is that decreasing the niobium content of an alloy makes it increasingly more difficult to produce a strictly single-phase alloy, regardless of quench rate. The instability of the BCC lattice results in either the formation of martensite, in the 20 and 25% Nb alloys, or the precipitation of the  $\omega$ phase. The effect of this instability is reflected in the resistivity and microhardness data.

The effect of microstructure on  $\rho$  and VHN is quite apparent in Figures 3.17, 3.18 and 3.19, particularly for the 20 and 25% Nb alloys. The  $\beta + \alpha$ " microstructure is much softer than the  $\beta + \omega$ microstructure. At room temperature the  $\beta + \alpha$ " and  $\beta + \omega$ microstructures effect similar resistivities; however, upon cooling to T<sub>c</sub>, the resistivities of the  $\beta + \alpha$ " alloys drop significantly, while those of the  $\beta + \omega$  alloys increase slightly. This effect of microstructure on the physical properties of Ti-Nb alloys has not been reported in the literature.

The compositional and quench rate dependence of VHN and  $\rho_0$  correlate well with the refinement of the  $\omega$  phase crystal structure. The abrupt upturn in the VHN vs composition curves coincides with the beginning of "virtual"  $\omega$  phase precipitation. As the precipitates become more "real", due to a decrease in either the niobium content of a specimen or the quench rate of the specimen, both VHN and  $\rho_0$  increase.

The temperature coefficient of  $\rho$  for the 30 - 70% Nb alloys also can be correlated with the refinement of the  $\omega$  phase crystal structure. Figure 3.18b shows that the gradual change from "virtual" to "real" precipitation with decreasing niobium content results in a monotonic decrease in  $\partial \rho/\partial T$ . A decrease in the quench rate for a given alloy produces the same effect, though to a much smaller extent.

The temperature dependence of P for the 20 and 25% Nb specimens in the AC and FC series may be interpreted in the following manner. (This interpretation is similar to those of Collings (COL74) and D'yakonova, et al. (DYA83).) The results of the present study demonstrate that an increase in the refinement of the  $\omega$  crystal structure results in an increase in  $\rho_0$  and a decrease in  $\partial \rho/\partial T$ . deFontaine, et al. (DEF71) and D'yakonova, et al. (DYA83) showed that this refinement could be produced by cooling a specimen to cryogenic temperatures. Therefore, decreasing the temperature of a specimen may result in an increase in  $\rho o$  and a decrease in  $\partial \rho / \partial T$ . If the effects of  $\omega$  structure refinement are great enough, a net negative value of ∂ρ/∂T may result (as was seen in the 20-AC, 25-AC and 25-FC specimens). The reversal of the sign of  $\partial \rho / \partial T$  upon cooling below 77K may be interpreted as indicating that the  $\omega$  crystal structure does not undergo further refinement, i.e. the  $(111)\beta$  planes have collapsed sufficiently to produce a fixed  $\beta$  +  $\omega$  microstructure.

The interpretation of this study is that  $\partial \rho / \partial T$  may be negative only in those alloys in which the structure of the  $\omega$  precipitates changes appreciably with decreasing temperature. The difference in  $\partial \rho / \partial T$  for the 20-AC and 20-FC specimens indicates that the microstructure of the 20-AC specimen changes on cooling, while that of the 20-FC specimen does not. (It will be recalled that diffusion during the FC quench resulted in a more complete collapse of the (111) $\beta$  planes.) That  $\partial \rho / \partial T$  is positive for most of the  $\omega$  containing specimens indicates that their microstructures do not change with decreasing temperature.

Between 77K and  $T_c \partial \rho / \partial T$  is positive for all specimens. The data of this study indicate that, in this temperature range, the minimum value of  $\partial \rho / \partial T$  is ~.0llu $\Omega$ -cm/K, regardless of alloy composition or specimen quench rate. This result is in agreement with the interpretation of this study.

In comparing the results of this study with those in the literature, there are both agreements and disagreements. The resistivity data of the literature are in general agreement with the data for the AC and FC series alloys of this study. There are disagreements regarding the interpretation of results with the studies of Hochstuhl and Obst (HOC82), and Chandrasekaran, et al. (CHA74).

The assumption by Hochstuhl and Obst that  $\omega$  precipitates did not form in their 22% Nb alloy until 80K is incompatible with the findings of the present study on two accounts. The results of the present study show that it is extremely difficult to produce a single-phase specimen of this composition. The present study also shows that the formation of  $\omega$  phase precipitates leads to an increase in the resistivity of an alloy, not a decrease. Their findings, however, can be interpreted using the mechanism proposed in the present study.

The determination by Chandrasekaran, et al. (CHA74) that a negative  $\partial \rho / \partial T$  is due solely to the BCC lattice instability, per se, and not to  $\omega$  phase precipitation is also at odds with the results of the present study. In light of the present study, their results may interpreted as follows. A negative  $\partial \rho / \partial T$  indicates that the stabilization process of the matrix, by way of "real" or "virtual"  $\omega$  phase precipitation, continues with decreasing temperature. That this was not seen in TEM demonstrates the difficulty of producing a bulk phase transformation in a very thin specimen. The positive  $\partial \rho / \partial T$  found after the isothermal precipitation of  $\omega$  in the same alloy can be explained by supposing that the precipitation which occurred during heat treatment stabilized the matrix and that the microstructure did not change further during cooling.

3.6 Results of the Present Investigation - Quenched and Aged Alloys

Determination of the stability limits of the isothermal  $\omega$  phase was the subject of this part of the present investigation. The specimens studied were air cooled to room temperature following recrystallization at 1000C. Fifteen minutes after removal from the 1000C furnace, the specimens were placed in another furnace and aged for 96 hours at temperatures between 300 and 500C. Only specimens of the 20 to 35% Nb alloys were heat treated and examined. The quenched and aged specimens fell into two groups -- those that formed  $\omega$  precipitates during isothermal aging (20 and 25% Nb), and those that didn't (30 and 35% Nb). The presentation of the results in this section is divided accordingly.

Two variations of this thermal processing were studied also. The effect of the rate of the intermediate quench was studied using the 20% Nb alloy. The effect of the presence of the intermediate quench was studied by directly aging specimens of the 20 to 35% Nb alloys at 400 and 500C for 96 hours.

#### 3.6.1 Microstructures of the 20 and 25% Nb Specimens

Isothermal precipitation of the  $\omega$  phase was observed in quenched specimens of the 20 and 25% Nb alloys that had been aged at 300, 350 and 400C for 96 hours. Representative dark field micrographs from the 20-AC-96/300 and 20-AC-96/400 specimens are shown in Figures 3.21a and b, respectively. These micrographs show that aging at higher temperatures results in larger precipitates. They also show that the matrix/precipitate interface is sharper at higher temperatures. This can be noticed especially at the narrow ends of the precipitates where they appear to fade into the matrix.

Several general features of  $\omega$  phase precipitation were observed in these specimens. The orientation relationships given in section 3.3.2 were confirmed. The  $\omega$  precipitate morphology was always one of an ellipsoid of revolution with the major axis parallel to  $\langle 0001 \rangle \omega$ 



FIGURE 3.21 Comparison of w precipitate size as a function of aging temperature (Dark field images) a) 20-AC-96/300, b) 20-AC-96/400

 $(\langle 111 \rangle \beta)$ . In addition, several manifestations of the subvariants described by Chang, et al. (CHA76) were observed. An attempt was made to determine the composition of the  $\omega$  precipitates using scanning transmission electron microscopy (STEM) and EDS, but the presence of the surrounding matrix precluded a reliable determination. Bright field images of these specimens showed that the  $\omega$  precipitates caused extensive strains in the BCC matrix. These strains, and the fact that no interfacial dislocations were evident, indicated that the  $\omega$ precipitates were coherent with the matrix. There was no evidence of a precipitate free zone at the grain boundaries.

The dimensions of the  $\omega$  precipitates as a function of aging temperature are given in Table 3.8. (In this table, 2a is the length of the major axis, 2b, the minor axis.) It was found that the precipitate size distributions were quite broad for all of the specimens examined. The lengths of the major and minor axes varied by as much as a factor of 2. The ratios of the two dimensions, however, were relatively constant. When the logarithm of 2a was plotted against 1/T, a straight line was obtained. An activation energy could not be determined because the time dependence of the precipitate growth was unknown.

Two additional 20-AC specimens were heat treated for 24 and 288 hours at 400C in order to study the growth kinetics of the  $\omega$ precipitates. The dimensions of the precipitates in these alloys are given in Table 3.9. During the first 24 hours of aging, the precipitates grew rapidly. Precipitate growth during the next 72

TAB	LE	3	•	8	

 $\boldsymbol{\omega}$  Precipitate Dimensions as a Function of Aging Temperature

<u>% Nb</u>	Temp	2a (nm)	2b (nm)	a/b
20 20 20	300 350 400	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{r} 6.1 + .9 \\ 11 + 2 \\ 30 + 4 \end{array}$	3.1 + .6 3.2 + .4 2.7 + .5
25 25 25	300 350 400	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3.1 + .3 3.3 + .4 3.0 + .5

Temperatures in Celsius Alloys AC quenched from 1000C to room temperature, then aged 96 hours

#### TABLE 3.9

 $\omega$  Precipitate Dimensions as a Function of Aging Time 20%~Nb

Time	<u>2a (nm)</u>	<u>2b (nm)</u>	a/b
AC	~15	~ 5	_
24	72 + 16	21 + 5	3.4 + .5
96	78 + 19	30 + 4	2.7 + .5
288	$133 \pm 40$	44 + 12	$3.0 \pm .5$

Times in hours

Alloys AC quenched from 1000C to room temperature, then aged at 400C

hours was very sluggish. Between 96 and 288 hours the precipitate dimensions increased approximately as t $^{1/2}$ .

Precipitation of the  $\alpha$  phase was found in the 20 and 25-AC specimens aged at 400C after 288 hours. In the 20-AC-288/400 specimen,  $\alpha$  phase reflections were detected in SAD patterns, while in the 25-AC-288/400 specimen,  $\alpha$  precipitates could be identified at the grain boundaries. Figure 3.22 is a micrograph from the 25-AC-288/400 specimen. This micrograph shows the coexistence of both  $\alpha$  and  $\omega$  precipitates in this specimen. The  $\alpha$  precipitates extended into the matrix only in particular crystallographic directions, behavior similar to that found at higher temperatures.

Isothermal aging at 450 and 500C resulted in precipitation of the  $\alpha$  phase in specimens of both alloys. Figure 3.23 shows an SAD pattern and bright field image from the 25-AC-96/450 specimen. The long axes of the  $\alpha$  precipitates in these alloys were found to be parallel to the <113> and <111> $\beta$  directions. Due to the complicated SAD patterns (see Appendix A), the presence of  $\omega$  phase precipitates could not be ruled out.

#### 3.6.2 Microstructures of the 30 and 35% Nb Specimens

The sequence of precipitation in specimens of the 30 and 35% Nb alloys was quite different from that in the 20 and 25% Nb specimens. The precipitates that will be shown do not resemble any shown in the literature.



FIGURE 3.22 Bright field image of the 25-AC-288/700 specimen showing  $\alpha$  precipitates at the grain boundary,  $\omega$  precipitates in the matrix



FIGURE 3.23 TEM micrographs showing  $\alpha$  phase precipitation in the 25-AC-96/450 specimen a) [110] SAD pattern, b) Bright field image

Heat treating for 96 hours at 300C resulted in faint  $\omega$  phase reflections in the SAD patterns of specimens of both alloys. The  $\omega$  precipitates in the 30-AC-96/30O specimen were ~5nm in length. The precipitates in the 35-AC-96/30O specimen were of the "virtual" type. Additional fine precipitation also was evident in bright field.

Aging at 350C produced precipitates which could be imaged, but which did not produce any extra reflections in SAD. Figures 3.24a - d show low and high magnification micrographs from both specimens. There appear to be two types of precipitate in the 30-AC-96/350specimen (Figures 3.24a and b). Faint  $\omega$  reflections in the SAD patterns could be used to form dark field images of the elongated precipitates which are 30 - 70nm in length. The long axes of these precipitates are parallel to <111> $\beta$ . The larger, nondescript precipitates are surrounded by strain fields. The appearance of these precipitates did not change appreciably with tilting.

Micrographs of the 35-AC-96/350 specimen are shown in Figures 3.24c and d. The appearance of the precipitates in these micrographs is unlike that of those in Figures 3.24a and b. These precipitates appear to have nucleated parallel to the  $\langle 001 \rangle$  and  $\langle 110 \rangle \beta$  directions. This directionality of nucleation did not appear to be related to dislocations which could be imaged by tilting slightly. The structure in the images of the precipitates was interpreted to be a single dislocation encircling each precipitate. This implies that these precipitates are semi-coherent with the matrix.



FIGURE 3.24 TEM micrographs showing precipitates in quenched and aged specimens of the 30 and 35% Nb alloys a and b) 30-AC-96/350, c and d) 35-AC-96/350

Aging specimens of these alloys for 96 hours at 400C produced precipitates similar to those shown in Figures 3.24a - d. The precipitates in both alloys had grown larger at the higher aging temperature. In the 30-AC-96/400 specimen there were still centers of localized strain. From these emanated dislocation loops and what appeared to be needle-shaped precipitates. These needles lay in the  $\langle lll \rangle \beta$  directions. As before, there were no additional reflections in the SAD patterns, though there were extremely faint and streaked  $\omega$ reflections. The precipitates in the 35-AC-96/400 specimen were still quite small, about 16nm in diameter, and appeared to be encircled by dislocations. There was one or two по indication of any directionality of precipitation as in the 35-AC-96/350 alloy.

Specimens of these alloys were aged for 288 hours at 400C also. The characteristic needles of  $\alpha$  precipitation were seen in the 30-AC-288/400 specimen. The SAD pattern of this specimen contained extremely faint  $\alpha$  reflections as well as faint and streaked  $\omega$  spots. A micrograph of the 35-AC-288/400 alloy is shown in Figure 3.25. The precipitates in this specimen grew with longer aging. An elongation of some of the precipitates in the <111> directions is evident while others appear to be encircled by more than one dislocation. SAD patterns showed only very weak  $\omega$  reflections in addition to the matrix spots.

Aging a 30-AC specimen for 96 hours at 450C allowed growth of the  $\alpha$  precipitates which resulted in an intensification of the  $\alpha$ 



FIGURE 3.25 Bright field image of the 35-AC-288/400 specimen

reflections in the SAD patterns. Aging at 500C produced still larger precipitates and very definite  $\alpha$  reflections in SAD.

Aging 35-AC specimens at 450 and 500C produced precipitates which still did not yield extra reflections in SAD. Examples of these precipitates, from the 35-AC-96/450 and 35-AC-96/500 specimens, are shown in Figures 3.26a and b, respectively. Increasing the aging temperature caused a coarsening of the precipitates and a decrease in their number density. The normals to the traces of the dislocations surrounding the precipitates in Figure 3.26b are parallel to the <111> $\beta$  directions. The dislocation spacing is ~7nm in the <111> $\beta$ directions.

3.6.3 Effect of Intermediate Quench Rate

It was shown in section 3.5 that, of the alloys of this investigation, the microstructure of the 20% Nb alloy was the most sensitive to quench rate. To determine if the rate of the intermediate quench affects the aged microstructure of this alloy, a 20% Nb specimen was fast water quenched to room temperature following recrystallization. This should have produced martensite in this specimen, though this was not verified. The specimen then was aged for 100 hours at 400C.

It was found that the 20-FW-100/400 specimen contained  $\omega$  phase precipitates of approximately the same dimensions as those in the



FIGURE 3.26 Bright field images of 35% Nb specimens a) 35-AC-96/450, b) 35-AC-96/500

20-AC-96/400 specimen. There was no evidence of  $\alpha$  phase precipitation in the 20-FW-100/400 alloy.

3.6.4 Microstructures of the Directly Aged Alloys

Specimens of the 20 to 35% Nb alloys also were aged for 96 hours at 400 and 500C without an intervening room temperature quench. These alloys were taken from the 1000C furnace and placed directly into another furnace. This series of heat treatments was executed to determine if the presence of an intermediate room temperature quench affected the microstructures of the aged alloys.

In Figures 3.27a and b are micrographs of the 20-AC-96/400 and 20-96/400 specimens. The effect of the presence of a quench prior to aging is striking. The intermediate quench enabled the  $\omega$  phase to grow to the exclusion of the  $\alpha$  phase, while direct aging produced  $\alpha$  precipitates to the exclusion of  $\omega$ . This effect has not been reported in the literature. The same effect was observed in the 25% Nb specimens.

The presence of an intermediate quench had no effect on the microstructures of the 30 and 35% Nb alloys aged at either 400 or 500C. An exception was that the precipitates in the 35-96/400 specimen appeared to nucleate in specific directions. The intermediate quench also did not significantly affect the microstructures of the 20 and 25% Nb alloys aged at 500C.



FIGURE 3.27 TEM micrographs showing the effect of a quench prior to isothermal aging a) 20-AC-96/400 ( $\beta$  +  $\omega$ ), b) 20-96/400 ( $\beta$  +  $\alpha$ )

As part of the investigation of the stable equilibria, specimens of all alloys were directly aged at 500C for 288 and 960 hours. precipitates were found in the 35-288/500 specimen. These precipitates produced reflections in the SAD patterns which could be used to form dark field images. Precipitates similar to those in the 35-AC-96/500 specimen were observed in the 40-96/500 and 40-288/500 the dislocations surrounding specimens. The spacing of the precipitates was 8 - 9nm in the former specimen, ~7nm in the latter. Aging the 50 and 60% Nb specimens for 960 hours at 500C produced precipitates similar to those in the 35-AC-96/400 specimen.

#### 3.6.5 Vicker's Hardness Numbers

The hardness data for the quenched and aged specimens are given in Table 3.10. They are plotted as a function of composition and aging temperature in Figures 3.28 and 3.29, respectively.

The hardness data for the specimens directly aged for 96 hours at 400C and 500C are given in Table 3.11. These data, as well as the corresponding data of the quenched and aged specimens, are plotted as a function of composition in Figure 3.30.

3.6.6 Discussion of the Results

A summary of the microstructures of the specimens which were air cooled to room temperature and then aged for 96 hours is given in

### TABLE 3.10

Vicker's Hardness Numbers of the Quenched and Aged Alloys

Temp	20	25	30	35
500	233	212	177	136
450	262	253	215	139
400	383	370	159	134
350	459	413	174	171
300	381	286	230	176

Temperatures in Celsius Compositions in at% Nb 100g load -- Typical Errors: 2% Alloys AC quenched from 1000C to room temperature, then aged 96 hours

#### TABLE 3.11

Vicker's Hardness Numbers of the Directly Aged Alloys

Temp	20	25	30	35
500	210	173	164	131
400	325	268	172	146

Temperatures in Celsius Compositions in at% Nb 100g load -- Typical Errors: 2% Aging Time: 96 hours



FIGURE 3.28 Vicker's hardness numbers of the quenched and aged specimens (data given in Table 3.10)



FIGURE 3.29 Vicker's hardness numbers of the quenched and aged specimens (data given in Table 3.10)



FIGURE 3.30 Vicker's hardness numbers showing the effect of a quench prior to isothermal aging (data given in Tables 3.10 and 3.11)

Table 3.12. Presented in this table are the second phases found in the specimens as a function of alloy composition and aging temperature.

Significant isothermal precipitation of the  $\omega$  phase was found in the 20 and 25-AC specimens aged at 300, 350 and 400C. This is in agreement with the data of the literature.  $\omega$  phase precipitates were not observed in any specimens aged above the metastable  $\omega \neq \beta$ transformation temperature of pure titanium.  $\omega$  phase precipitation in the quenched and aged 20% Nb alloys was found to be insensitive to the rate of the intermediate quench.

Very little  $\omega$  phase precipitation appeared to occur in quenched and aged specimens of the 30% Nb alloy. Precipitates similar in size to those in the 25-AC specimen were produced in the 30-AC-96/300 30-AC specimen specimen. Aging a 96 hours at 350C yielded precipitates, the long axes of which were twice as long as those in the 20 and 25-AC specimens aged 96 hours at 350C. In addition, the density of precipitation in the 30-AC-96/300 specimen was significantly less than that in the corresponding 20 and 25% Nb The 30% Nb alloy contained the highest oxygen content, specimens. 3821appm, of any of the alloys used in this investigation (see Table 2.3). It was presented in the review of the literature that interstitial oxygen suppresses the formation of the  $\omega$  phase and promotes the growth of a. Thus, the possibility exists that isothermal  $\omega$  phase precipitation in this alloy was suppressed; however, an enhancement of a phase precipitation was not observed.

TAB	LE	3.	12

Second Phases in the Quenched and Aged Alloys

Temp	_20	25		35
500				0
500	α	α	α	<i>:</i>
450	α	α	α	?
400	ω	ω	?.	?
350	ω	ω	?	?
300	ω	ω	ω	-

Temperatures in Celsius Compositions in at% Nb Alloys AC quenched from 1000C to room temperature, then aged 96 hours

.

.
For these reasons, it is uncertain that isothermal  $\omega$  phase precipitates may form in a 30% Nb alloy.

The growth kinetics of  $\omega$  phase precipitation were studied in specimens of the 20% Nb alloy. The kinetics were difficult to determine because of the broad distribution of precipitate sizes. The temperature dependence was found to be in agreement with that determined by Morniroli and Gantois (MOR73). The time dependence, however, was unlike that determined by either Morniroli and Gantois (MOR73) or Lyon (LYO81).

In order to determine the  $\omega$  growth kinetics, it was necessary to measure the dimensions of the  $\omega$  precipitates. These measurements were difficult and subject to errors for the following reasons. As shown in Figure 3.21a, the precipitate/matrix interface was not well defined at low temperatures. In addition, long exposures, e.g. 45 to 90 seconds, were necessary to record images on film. Building vibrations made it necessary to work late at night and to limit magnifications to 200,000x in order to obtain usable micrographs under these exposure conditions.

The presence of an intermediate quench noticably affected the aged microstructures only in specimens of the 20 and 25% Nb alloys aged at 400C. In these alloys, a room temperature quench before aging resulted in precipitation of the  $\omega$  phase to the exclusion of the  $\alpha$  phase. Eliminating this quench enabled  $\alpha$  precipitates to grow to the exclusion of  $\omega$  precipitates. This marked effect on microstructure has not been reported in the literature.

Varying the rate of the intermediate quench did not affect the microstructures of quenched and aged 20% Nb specimens. This indicated that the difference in the quenched and aged and directly aged microstructures was due to changes which occurred during the reheating of the specimen following the intermediate quench.

The reason why a quench prior to aging affects the aged microstructures of the 20 and 25% Nb alloys is uncertain. It may be argued that the reheating of a specimen results in a lower than equilibrium vacancy concentration at the aging temperature, while directly aging the specimen results in a vacancy supersaturation at the aging temperature. If this were the case, however, the effects would be very short-lived and would not be expected to produce the observed results. This phenomenom, therefore, awaits further investigation.

Precipitation of the  $\alpha$  phase was found in several of the quenched and aged specimens.  $\alpha$  precipitates were found in the 20, 25 and 30-AC specimens after aging 288 hours at 400C. (It will be recalled that  $\alpha$ phase precipitation was present in the directly aged specimens of the 20 and 25% Nb alloys after only 96 hours at 400C.) Aging these specimens at 450 and 500C produced  $\alpha$  precipitates after 96 hours. Recognizable precipitation of the  $\alpha$  phase occurred in specimens of the 35% Nb alloy only after aging 288 hours at 500C. In most of these specimens, the appearance of  $\alpha$  precipitates in bright field images was not immediately accompanied by the appearance of  $\alpha$  reflections in SAD.

When  $\alpha$  reflections were observed in SAD, the Burger's orientation relationships were confirmed.

The long axes of the a precipitates were determined to be parallel to the <113>B directions. When the electron beam passing through a specimen was parallel to the [110] & direction, the long axes of the  $\alpha$  precipitates were observed to be parallel to the <113> and  $\langle 111 \rangle \beta$  directions. The long axes of the precipitates were parallel to the  $\langle 110 \rangle \beta$  directions when the specimens were in a [111] $\beta$  orientation. Using the [110] and [111] cubic stereograms shown in Appendix C, it was found that the long axes of the precipitates were, in fact, parallel to the  $\langle 113 \rangle \beta$  directions. For a precipitates obeying the Burger's orientation relationships, the  $\langle 113 \rangle \beta$  directions are parallel to the normals of the  $\{\overline{1}100\}\alpha$  planes. Williams (WIL73) stated that the long axes of the  $\alpha$  precipitates were parallel to the  $\langle 110 \rangle \beta$ directions. This is compatible with the results of the present study if Williams observed  $\alpha$  precipitates only in a [111] $\beta$  orientation.

The microstructures produced by aging the 30 and 35-AC specimens were unlike any in the published literature. The precipitates did not give rise to any extra reflections in SAD, though in all of the samples very faint and streaked  $\omega$  reflections were observed. No other information could be determined about the nondescript precipitates in the aged 30-AC specimens.

It is believed that the precipitates in the aged 35-AC specimens are not  $\beta$  precipitates for the following reason. The spacing of the dislocations encircling the precipitates shown in Figures 3.26b is

approximately 7nm in the <lll> $\beta$  directions. The maximum difference in  $\beta$  phase lattice parameter in the Ti-Nb system is about 1.7pm (see section 4.5.2). For this difference in lattice parameters, the 193rd {lll} plane in the matrix would just match the 192nd {lll} plane in a  $\beta$  precipitate. This implies a dislocation spacing of about 37nm, not 7nm. For the more realistic case of .3pm difference in the lattice parameters, the dislocation spacing would be about 1200nm.

By the same reasoning, it can be argued that these precipitates are a nuclei. The fact that prolonged aging at 500C results in recognizable  $\alpha$  precipitates supports this argument. The  $\{\overline{1}2\overline{1}0\}\alpha$ planes are parallel to the  $\{111\}\beta$  planes. The d-spacing of the  $\{111\}$ planes is almost twice that of the  $\{\overline{1}2\overline{1}0\}$  planes. Thus, every other  $\{\overline{1}2\overline{1}0\}$  plane matches every  $\{111\}$  plane, with the exception that instead of the 56th {111} plane matching the 112th  $\{\overline{1210}\}$  plane, the This results in a dislocation spacing in the <111> 57th matches. directions of about llnm, fairly close to the observed 7nm. Schematics of the matching of the  $\beta$  and  $\alpha$  precipitates with the matrix are shown in Figure 3.31. If the precipitates in the aged 35-AC specimens are actually  $\alpha$ , it is unknown why they remain relatively small and semi-coherent instead of developing the expected needle-shaped morphology. It is also unknown why they did not produce extra reflections in SAD.

The effects of microstructure on the hardness values of the quenched and aged specimens are demonstrated in Figures 3.28 and 3.29. Specimens which contain  $\omega$  phase precipitates are significantly harder



FIGURE 3.31 Schematic of the lattice matching of the  $\beta$  matrix with two precipitates a)  $\alpha$ , b)  $\beta^{\star}$ 

than those which contain  $\alpha$  precipitates. The larger the precipitates, though, the lesser the hardening effect. In those alloys in which increasing the aging time or temperature leads to precipitation of the  $\alpha$  phase, the hardness values decrease accordingly.  $\alpha$  precipitation in the 30-AC-96/450 specimen leads to an increase in hardness. This shows that a  $\beta$  +  $\alpha$  microstructure is harder than a  $\beta$  microstructure, but not as hard as a  $\beta$  +  $\omega$  microstructure. The precipitates in the 35% Nb alloy had a slight effect on the hardness of that alloy, but again, as the precipitates coarsen, the hardness of that alloy decreases.

The hardness values of the quenched and aged and directly aged specimens are compared in Figure 3.30. The effect of a quench prior to aging is marked, and previously unmentioned in the literature. As seen before, a  $\beta + \omega$  microstructure is much harder than a  $\beta + \alpha$  microstructure. The differences in the hardness values of the specimens aged at 500C may be attributed to the sizes of the  $\alpha$  precipitates.

#### 3.7 Summary

The microstructural results of this part of the present study are summarized in the metastable phase diagram shown in Figure 3.32. As will be demonstrated in Chapter 4, this entire metastable phase diagram lies within the  $\alpha + \beta$  two-phase region of the equilibrium phase diagram. This point is reinforced by the fact that prolonged



FIGURE 3.32 Metastable phase diagram. Shaded area indicates where athermal  $\omega$  precipitates have been detected.  $\beta + \omega$  boundary is based on aging quenched alloys for 96 hours.

aging of most of the specimens of this study resulted in precipitation of the  $\alpha$  phase.

A martensitic transformation was found to occur only in specimens of the 20 and 25% Nb alloys, and then only for those which received the fastest quench to room temperature. Evidence of a martensitic transformation below room temperature in other specimens could not be produced.

A definite upper composition limit for the formation of athermal  $\omega$  phase precipitates was not found in the specimens of this study. It was shown that the  $\omega$  precipitates in the quenched alloys gradually changed from "real" to "virtual" with increasing niobium content. For this reason, most Ti-Nb alloys at room temperature are not, in the strictest sense, single-phase. It was also proposed that the athermal  $\omega$  phase precipitation process may continue in some alloys when cooled below room temperature.

The stability limits of the formation of isothermal  $\omega$ precipitates, on the other hand, are relatively definite, but depend on aging time and prior thermal history. The limits shown in Figure 3.31 are for quenched alloys aged for 96 hours. It was shown that increasing the aging time or eliminating the room temperature quench prior to aging causes the isothermal  $\omega$  field to shrink. Decreasing the aging time may broaden this field.

CHAPTER FOUR

## STABLE EQUILIBRIA

### CHAPTER FOUR

### STABLE EQUILIBRIA

## 4.1 Introduction

In the nine (Ti, Zr, Hf) - (V, Nb, Ta) binary alloy systems, three types of equilibrium phase diagrams have been observed. The phase diagram type correlates well with the difference in atomic volume of the constituent elements. In the Zr-V and Hf-V systems this difference is  $\geq 60\%$  and the phase diagrams are characterized by the intrusion of an intermetallic compound with a composition of 66.7% V. The atomic volume difference is between 20 and 30% in the five systems in which there is a stable  $\beta$  phase miscibility gap. These alloy systems are monotectoid in nature. In the Ti-Nb and Ti-Ta systems, the atomic volume difference is only about 2%. On the basis of the existing data, it appears that these two systems are  $\beta$ -isomorphous.

There are two stable phases in the titanium-niobium alloy system. They are  $\alpha$ , which is hexagonal close-packed (HCP), and  $\beta$ , which is body-centered cubic (BCC). Pure titanium is polymorphic, as was shown in Figure 3.5. Above 882.5C,  $\alpha$ -Ti is unstable with respect to  $\beta$ -Ti at atmospheric pressure. Pure niobium is BCC.

The complete low temperature equilibrium phase diagram has not been determined experimentally, though several general features have been elucidated. Above 882.5C there is complete solubility in the  $\beta$  phase. Below this, the solubility of niobium in  $\alpha$ -Ti is very limited, the maximum solubility being 1 - 2% Nb. Between these two single-phase regions is a broad two-phase region in keeping with the  $\beta$ -isomorphous classification.

There have been several calculations of the Ti-Nb phase diagram. Some have been based on thermodynamic data, others on the experimental phase diagram data. All calculations agree as to the type of phase diagram, but differ by several hundred degrees as to the positions of the boundaries.

This part of the present study was begun in an attempt to better understand the equilibrium phase diagram. Because of the small diffusion coefficients in this system, it was not expected that equilibrium would be achieved in the alloys of this study. It was anticipated, however, that these results could be used to provide information concerning the kinetics of the  $\beta$  phase decomposition and to confirm the predictions of the phase diagram calculations.

There are two primary factors which affect the positions of the phase boundaries in the Ti-Nb alloy system -- these are alloy composition and interstitial content. Alloy composition has a two-fold effect. Increasing the niobium content of an alloy heat treated in the two-phase region decreases the amount of  $\alpha$  phase that will be precipitated. In addition, the diffusion coefficient decreases exponentially with increasing niobium content (see section 4.2.4). Thus, increasing the niobium content of an alloy not only significantly retards the establishment of equilibrium in the alloy, it also makes it more difficult to observe.

Not studied in the present investigation, but of importance, were the effects of interstitial contamination. As in the literature of Chapter 3, few studies have reported the interstitial contents of their alloys, giving instead the impurities in the starting materials. Interstitial analyses for the alloys of the present study were given in section 2.2.

In order to hasten the kinetics of the phase transformations, the alloys used in past studies had been cold-worked. In contrast, the alloys of the present study were examined in a recrystallized state. This was done to facilitate the interpretation of TEM results and the correlation of the results of this chapter with those of Chapter 3. The four specimens heat treated at 500C for 3696 hours (154 days), however, had not been recrystallized.

The outline of this chapter is as follows. First, a review of the pertinent literature is given. This is followed by a presentation and discussion of the results of the present investigation.

4.2 The  $\alpha$  and  $\beta$  Phases

As noted earlier, there are two stable phases in the Ti-Nb system --  $\alpha$  and  $\beta.$  The  $\alpha$  phase is the low temperature, low pressure phase of

pure titanium (see Figure 3.5). In Ti-Nb alloys, there is very limited solubility of niobium in  $\alpha$ -Ti, the maximum solubility being 1 - 2% Nb (HAN51, IMG61, RON70).

Above 882.5C, all alloys are in the single-phase  $\beta$  region of the phase diagram. Quenching from this phase field preserves the  $\beta$  phase structure in alloys with compositions greater than ~25% Nb. Thus, any precipitation that occurs in this alloy system does so in a BCC matrix.

4.2.1 The a Phase Crystal Structure and Orientation Relationships

The lattice parameters of pure  $\alpha$ -Ti are given in Table 4.1. These do not vary appreciably upon alloying with niobium (JEP70, MOR73).

The effects of interstitials on the  $\alpha$ -Ti lattice parameters are given in Table 4.2. It can be seen that the c parameter is more sensitive to impurities than the a parameter.

In Ti-Nb alloys, the  $\alpha$  phase precipitates from the  $\beta$  phase matrix during isothermal aging. The resultant precipitates follow the BCC/HCP Burger's orientation relationships which are:

(0001) α || (011) β <1120> α || <111> β

## TABLE 4.1

## Lattice Parameters of $\alpha$ -Ti

<u>a (nm)</u>	<u>c (nm)</u>	c/a	Ref
•29504 •29506	•46833 •4686	1.5873 1.5882	PEA58 RUD69
.29479	.46832	1.5887	FR076

## TABLE 4.2

# Effect of Interstitials on the $\alpha$ -Ti Lattice Parameters (from FR076)

Element	<u>∆a</u>	_∆c
С	.0003	.0013
N	-	.0007
0	.0000 <b>9</b>	•0004
н	.011	.06

.

.

All values in nm/at%

### 4.2.2 a Precipitate Morphology

In titanium-based alloys in which the  $\alpha$  phase precipitates directly from the BCC matrix, two morphologies of  $\alpha$  precipitates have been observed (WIL73). ( $\alpha$  precipitate morphology has not been studied in the Ti-Nb system.) The first is a Widmanstätten type which forms as plates or needles, the long axes of which are parallel to {110} $\beta$ . Precipitates which form in this manner obey the Burger's orientation relationships.

The second type of precipitate morphology is that of aggregates of very small  $\alpha$  precipitates (WIL73). These precipitates form either rafts of nondescript size and shape, or long, lenticular regions. An increase in the amount of precipitation occurs by growth of the aggregate regions, the individual precipitates remaining constant in size. This type of precipitation does not appear to obey the Burger's relationships. This precipitate morphology was found in alloys with a high concentration of the  $\beta$  stabilizing element.

### 4.2.3 The $\beta$ Phase Lattice Parameters

Pure niobium, and all Ti-Nb alloys above 882.5C possess the β phase, BCC structure. The lattice parameter for pure niobium is given in Table 4.3. The effects of interstitial impurities on this value are given in Table 4.4.

## TABLE 4.3

Lattice Parameter of  $\beta$ -Nb

Ref
HAN51
PEA58
HIC69a
RUD69
FR076

.

.

.

## TABLE 4.4

Effect of Interstitials on the  $\beta\text{-Nb}$  Lattice Parameter

Element	<u>∆a</u>	
С	.00044	
N	.0005	
0	.00041	
Н	.00023	

All values in nm/at%

•

The  $\beta$  phase lattice parameter decreases with decreasing niobium content, but only very slightly. The lattice parameter of  $\beta$  phase Ti-Nb alloys has been measured by Hansen, et al. (HAN51), Hickman (HIC69a), and Rudy, et al. (RUD69). The data are shown in Figure 4.1.

The alloys x-rayed by Hansen, et al. (HAN51) were the same ones used in their determination of the phase diagram (see section 4.3). The alloys x-rayed, however, received additional homogenization heat treatments. Powders from these alloys were sealed in titanium capsules and annealed for one hour at 860C. They were x-rayed with Cu radiation in a Debye-Scherrer camera. In several films there were low angle lines not belonging to the BCC structure which could not be identified. In their graph of the lattice parameters, it was stated that the units of measure were angstroms, though according to Pearson (PEA58), they were actually kX. Therefore, the data of Hansen, et al. have been multiplied by 1.002063 to convert them for plotting in Figure 4.1.

Rudy, et al. (RUD69) published no details regarding their x-ray technique, but it is known that their niobium powder was produced by first hydriding pure niobium, powdering the hydride, and then dehydriding the powder. This may explain their rather large lattice parameter value for pure niobium.

Hickman (HIC69a) used the Bond technique (BON60) to determine the  $\beta$  phase lattice parameters. The x-ray specimens were strips cut from 1.6mm sheet which were annealed between 1200 and 1300C in an ultra-high vacuum for several hours, and then quenched with He gas.



FIGURE 4.1  $\beta$  phase lattice parameters (from the literature)

The Bond technique requires that the position of just one high angle reflection from a single-crystal specimen be measured on both sides of the primary x-ray beam. (This is in contrast to the more common method of measuring several reflections from a powder specimen and extrapolating to  $\theta = 90^{\circ}$  to find a.) This technique can have a precision of  $\pm 000$  (BON60), although Hickman stated an error of  $\pm 000$  m.

Table 4.4 shows that interstitial contamination results in an increase in the lattice parameter of pure niobium. Similar effects would be expected in  $\beta$  phase Ti-Nb alloys. Because of the very high temperature heat treatments given the specimens of Hickman, it is quite possible that they became contaminated. This could account for the differences in the lattice parameter values of Hickman and Hansen, et al. for alloys with more than 30% Nb.

The data of Hansen, et al. (HAN51) show a minimum in the lattice parameter at 34.6% Nb. Below 40% Nb, the data of Rudy, et al. (RUD69) show little variation with alloy composition. It is not known if these results were real, i.e. the two phase field had been entered, or just artifacts of specimen preparation or alloy fabrication.

4.2.4 Diffusion in the  $\alpha$  and  $\beta$  Phases

Since  $\alpha$  precipitates form in a  $\beta$  matrix, their nucleation and growth kinetics will be dependent upon diffusion in the  $\beta$  phase. In an alloy, the diffusion coefficient of interest is the interdiffusion

This diffusion coefficient was measured by Roux and coefficient. Vignes (ROU70) using Ti/Nb and Ti-Nb/Nb diffusion couples. The data were analyzed according to the Matano method. Their data showed that temperature decreased interdiffusion coefficient any the at exponentially with increasing niobium content. Unfortunately, there were not enough data to derive an empirical expression for the a function of composition and interdiffusion coefficient as temperature.

There have been several studies of  $^{95}$ Nb tracer diffusion in pure titanium (GIB63, ASK65, PON79), pure niobium (RES60, PEA62a, LUN65, MEH71, ABL77, EIN78) and in several Ti-Nb alloys (PEA62, GIB63, PON79). Careful measurements and analyses have shown that diffusion in  $\beta$ -Ti (GIB63, ASK65) and in pure niobium (MEH71, EIN78) is anomalous. Instead of being described by:

$$D = D \exp(-Q/RT)$$

diffusion in the BCC refractory metals is better described by:

$$D = D_1 \exp(-Q_1/RT) + D_2 \exp(-Q_2/RT)$$

There are several theories about and discussions of this anomalous diffusion behavior in the literature. While they may be of interest, they are not germane to this thesis. With the exceptions noted above, tracer diffusion in the Ti-Nb system has been analyzed in the literature according to the traditional Arrhenius model.

The data for <sup>95</sup>Nb tracer diffusion are shown in Figures 4.2a and b. For the purposes of this study, these data have been fit with the straight lines shown in these figures. The data of RES60, PEA62,



FIGURE 4.2a Exponential pre-factor for niobium tracer diffusion (from the literature)



FIGURE 4.2b Activation energy for niobium tracer diffusion (from the literature)

PEA62a, GIB63, LUN65, ABL77, and PON79 were used in the calculations of these lines. The data fitted with the double exponential, and three other data points (0% Nb (GIB63), and 20 and 36% Nb (PON79)) were not included in these calculations. The diffusion coefficients thus determined were:

$$D = D_{o} \exp(-Q/RT)$$
  

$$D_{o} = 5.5783 \times 10^{-4} \exp(8.209 x) \qquad cm^{2}/sec$$
  

$$Q = 31,463 + 65,674 x \qquad cal/mole$$

where x is the atomic fraction of niobium in an alloy.

There have been a few studies of titanium diffusion in the Ti-Nb system. These data are compiled in Table 4.5. The data not only show the same composition dependence as does the <sup>95</sup>Nb tracer data, they also are close in value to the Nb tracer data.

When the components of the diffusion coefficients given above were used to calculate diffusion coefficients in alloys, the results usually were less than a factor of 3 different from the interdiffusion coefficients measured by Roux and Vignes (ROU70). (The calculated diffusion coefficients were always lower than those measured.) This good agreement must be due to the similarities in the diffusion coefficients of both niobium and titanium in this system.

In Figure 4.3 are plotted values of the calculated diffusion coefficient as a function of temperature and composition. This figure illustrates the dramatic drop in diffusivity as the niobium content of an alloy is increased. For example, at 500C, the diffusion coefficients of 20 and 70% Nb alloys differ by about 8 orders of

TABLE	4	•	5
-------	---	---	---

Titanium	Diffusion	in	Ti-Nb	Alloys
----------	-----------	----	-------	--------

<u>% Nb</u>	Do	Q	Ref
0	.000454	31,300	PON79
0	.0019	36,500	WAL68
5.4	.00127	35,610	PON79
19.6	.00315	41,960	PON79
35.7	.251	59,020	PON79
100	•1	86,930	PEL70
100	• 4	88,500	R0U70
	2		

 $D_o \text{ in } \text{cm}^2/\text{sec}$ , Q in cal/mole



FIGURE 4.3 Calculated niobium diffusion coefficients (based on the data in Figures 4.2a and b)

magnitude. This implies that if it were possible to reach equilibrium in the 20% Nb alloy in 3 seconds at 500C, the 70% Nb alloy would be reaching equilibrium in about 10 years.

The self-diffusion coefficient of titanium in the vicinity of the  $\alpha + \beta$  transformation was studied by Libanati and Dyment (LIB63) and Walsoe de Reca and Libanati (WAL68). It was found that the diffusion coefficient fell ~2.5 orders of magnitude upon the transformation of  $\beta$ -Ti to  $\alpha$ . The self-diffusion coefficient in  $\alpha$ -Ti was measured to be (LIB63):

$$D = 6.4 \times 10^{-8} \exp(-29300/RT)$$
  $cm^2/sec$ 

Since niobium is not very soluble in  $\alpha$ -Ti, it would be expected that diffusion in an  $\alpha$  precipitate would be similar to that in  $\alpha$ -Ti.

The composition of an alloy for which the diffusion coefficients for the  $\alpha$  and  $\beta$  phases are equal can be computed using the above equations. A plot of these compositions is shown in Figure 4.4. For alloys to the left of this line diffusion in the  $\beta$  phase is faster than in the  $\alpha$  phase. The opposite is true to the right of this line.

4.3 Metallurgical Investigations of the Phase Diagram

The data for the  $\alpha/\beta$  phase boundaries are shown in Figure 4.5. The data of Brown, et al. (BR064, BR066) are for the  $\beta$  transus, but lie below the other data for reasons to be discussed later. The  $\alpha$ transus is susceptible to scatter because of the low solubility of



FIGURE 4.4 Comparison of diffusion coefficients in the  $\alpha$  and  $\beta$  phases. To the left of this line, niobium diffusion in the  $\beta$  phase is faster than titanium diffusion in the  $\alpha$  phase. The opposite holds to the right of this line.



FIGURE 4.5 Experimentally determined phase boundaries (from the literature)

niobium in  $\alpha$ -Ti. In the following review, all alloys were arc melted with a non-consumable tungsten electrode.

Hansen, et al. (HAN51) used iodide titanium sheet (15-800 appm 0 and N) and niobium powder compacts as the raw materials for the alloys used in their phase diagram determination. Ingots of 5 to 30g were melted and inverted at least three times. It is not clear that the ingots were homogenized after melting. The ingots were cold-compressed and cold-rolled approximately 70%. At this point, the alloys used to determine the  $\beta$  transus at 700C and below were sealed in titanium capsules and homogenized for 20-40 hours at 1250C. The alloys used to determine the  $\alpha$  transus, and the  $\beta$  transus above 700C were not homogenized prior to the final heat treatment. The final heat treatments were performed in evacuated Vycor capsules. Heat treatment times ranged from 135 hours at 828C to 648 hours at 600C. The alloys were examined under a light microscope to determine their microstructures.

Hansen, et al. report that above 750C the  $\beta$  transus could be determined with certainty. All the alloys annealed at 700, 649 and 600C, however, showed small amounts of precipitation. This was attributed to residual coring, even though these alloys had been homogenized prior to their final heat treatments. No alloys were heat treated below 600C as it was thought that equilibrium was practicably impossible to achieve.

In the study of Imgram, et al. (IMG61), alloys were made of electrolytically refined titanium granules (325 appm 0, 170 appm N,

3770 appm H) and electron-beam melted niobium rod. The 250g ingots were inverted and melted twice. The ingots were hot-forged in air, at 925-980C, into 19mm diameter rods. The scale formed at this step was removed by sand blasting. The rods were then vacuum annealed for 6 hours at 980C to lower the hydrogen content. Following this anneal, the rods were hot-swaged, at 600 to 700C, to a diameter of 6.4mm and descaled again. The as-swaged chemical analyses were 690-1590 appm 0 and 625-1045 appm H. No times were given for the final heat treatments which were carried out in Vycor capsules filled with argon. The alloys were examined under a light microscope.

Ronami, et al. (RON70) used a diffusion layer method coupled with x-ray microanalysis to determine the phase boundaries. Iodide titanium, pure niobium and a 37.7% Nb alloy were used in this study. Discs cut from the pure metal and alloy rods were welded together under pressure, forming an  $\alpha/\beta$  diffusion couple of Ti/Nb, or Ti/37.7% Nb. The diffusion couples were vacuum annealed at 800C (500 hours), 700C (600 hours) and 650C (900 hours). The diffusion layers were analyzed with an electron probe microanalyzer with an estimated accuracy of 1 wt%. The  $\alpha$  solid solution layer was narrow, making it difficult to determine the maximum niobium concentration in  $\alpha$ -Ti to this accuracy.

The last study of the  $\alpha/\beta$  phase boundaries to be presented is that of Brown, et al. (BR064, BR066). The resistance as a function of temperature was used to determine the  $\beta$  transus. High purity titanium sponge and high purity niobium sheets were used as the starting

Ingots of 25g were melted three times, and then materials. homogenized for 24 hours at 1000C. The ingots then were hot-forged into 2mm thick plates; prior to forging they were heated in an argon atmosphere, rather than in air, in order to minimize contamination. Measurements of hardness as a function of distance from the surface showed that the contamination from air was limited to a layer .2mm Accordingly, a layer this thick was removed from the surface thick. of the alloys following any high temperature exposure to air. The made, under vacuum, at discrete resistance measurements were The temperature intervals were 25C or less. The time temperatures. allowed for equilibration at each temperature was not given.

To confirm their results, Brown, et al. (BR066), performed a light metallography study. The samples for this study were 0.5mm thick and were heat treated in vacuum. They were first heated for 15 minutes at 800C, then slowly cooled to 25C above or below the  $\beta$  transus determined by the resistance method and held there for 30 minutes to 5 hours. The samples aged 25C above the  $\beta$  transus showed some precipitation at the grain boundaries, though significantly less than those aged 25C below the boundary. The amount of the second phase remained constant as the aging temperature was raised to 150 to 200C above the  $\beta$  transus; above this, no precipitation was observed. This second phase was attributed to impurities, notably nitrogen.

The data for the  $\beta$  transus of Hansen, et al. (HAN51), Imgram, et al. (IMG61) and Ronami, et al. (ROM70) are in fairly good agreement

with each other. Decreasing diffusivity would appear to be the cause of the uncertainty below 700C in the data of Hansen, et al.

The small diffusion coefficients in this alloy system would appear to be the reason that the data of Brown, et al. (BR064, BR066) fall so far below those of the others. The heat treatments of the other investigations were several hundred hours long. It may be assumed that Brown, et al. did not wait this long at each temperature. Their resistance data show that increasing the niobium content of a specimen results in a smaller increase in resistance when the phase boundary is crossed. This indicates that the amount of  $\alpha$  phase precipitated decreases with increasing niobium content. This effect may be attributed to the effects of diffusion. Thus, the data of Brown, et al. may be assumed to be non-equilibrium in nature.

That the  $\beta$  transus determined by Brown, et al. is below the actual transus is reinforced by the fact that when their specimens were aged 150 to 200C above their  $\beta$  transus, precipitation resulted. Aging at even higher temperatures, however, did not produce any precipitation. Refering to Figure 4.5, it is found that these results are in agreement with the other  $\beta$  transus determinations.

## 4.3.1 Effect of Interstitials

Khaled, et al. (KHA81) have shown theoretically that carbon, nitrogen and oxygen in solution lower the free energy of the  $\alpha$  phase relative to the  $\beta$  phase. The predicted effect of this on the  $\beta$ 

transus is shown in Figure 4.6. This effect was demonstrated experimentally by Hansen, et al. (HAN51) in the Ti-Mo system. Alloys were prepared using titanium of two different purities. The low purity titanium contained 793 appm C, 238 appm N, 4165 appm 0 and 2833 appm H (analyses were not given for the higher purity, iodide titanium). The  $\beta$  transus determined with the low purity alloys was about 20C higher than that determined with the high purity alloys.

Examination of the Ti-H phase diagram (HAN58) shows that hydrogen in solution stabilizes the  $\beta$  phase over the  $\alpha$  phase. This would result in a lowering of the  $\beta$  transus. The Nb-H phase diagram (SHU69) shows that sufficient hydrogen in solution can lead to a BCC miscibility gap.

### 4.4 Phase Diagram Calculations

There have been two calculations of note of the Ti-Nb phase diagram. Regular-solution calculations were made by Kaufman and Bernstein (KAU70) and Murray (MUR81, MUR84). (The equations of the regular solution model are given in Appendix D.) The results of these calculations are shown in Figure 4.7 together with the experimental data for the phase boundaries. Figure 4.8 shows both calculations of the entire low temperature phase diagram. The lattice stability parameters used in these calculations are given in Table 4.6, the interaction parameters, in Table 4.7.



FIGURE 4.6 Effect of interstitials in solid solution on the  $\beta$  transus (from KHA81)



FIGURE 4.7 Comparison of the experimental phase diagram data with the calculations of KAU70 and MUR84



FIGURE 4.8 Comparison of the calculated phase diagrams
## TABLE 4.6

Lattice Stability Parameters (from KAU70)  $\Delta G_{Nb}^{\beta + \alpha} = 1500 + .8T$  $\Delta G_{Ti}^{\beta + \alpha} = -1050 + .91T$  $\Delta G_{Ti}^{\beta + \omega} = -690 + .99T$  $\Delta G_{Ti}^{\alpha + \omega} = 360 + .08T$  $\Delta G^{\circ}s \text{ in cal/mole}$ 

## TABLE 4.7

Regular Solution Interaction ParametersPhaseKAU70MUR81MUR84

	·····		
α	3125	598	2438
β	3125	-1127	1243

In cal/mole

The calculations of Kaufman and Bernstein (KAU70) were part of a phase diagram calculation tour-de-force. In general, the regular solution parameters were determined from existing experimental data. When there were no data, the parameters were estimated. For the Ti-Nb system, the lattice stability parameters for titanium were determined from the P-T phase diagram of pure titanium. The lattice stability parameter for niobium was estimated on the basis of the behavior of neighboring elements. The interaction parameters were derived essentially from "first principles." It is important to note that none of the parameters used by Kaufman and Bernstein were determined from the existing Ti-Nb phase diagram data. Nonetheless, their calculations agree well with the data of Hansen, et al. (HAN51), Imgram, et al. (IMG61) and Ronami, et al. (RON70).

The calculations of Murray (MUR81, MUR84) were part of the ASM/NBS phase diagram project. The lattice stability parameters of Kaufman and Bernstein were used in these calculations, though different sets of interaction parameters were used. Initially (MUR81), the interaction parameters were chosen so that the calculations fit the data of Brown, et al. (BRO64, BRO66). The resultant negative  $\beta$  phase interaction parameter was acknowledged (MUR81) as being physically unreasonable in this system. A later modification (MUR84) placed the  $\beta$  transus between the experimental data.

All of the Ti-Nb phase diagram calculations agree as to the type of phase diagram, i.e.  $\beta$ -isomorphous. The calculations of the  $\beta$ 

transus, however, differ by several hundred degrees. This discrepancy indicates that more experimental data are needed.

4.5 Results of the Present Investigation

Phase transformations in the vicinity of the  $\beta$  transus were studied using the alloys and aging temperatures shown schematically in Figure 4.9. Specimens were recrystallized at 1000C and then directly aged for 96, 288 and 960 hours (4, 12 and 40 days respectively). For comparison, Hansen, et al. (HAN51) aged their specimens 300 hours at 700C, 648 hours at 600C. Ronami, et al. (RON70) used aging times of 600 hours at 700C, 900 hours at 650C. Also shown in this figure are the phase diagram calculations of Kaufman and Bernstein (KAU70) and Murray (MUR84).

The precipitation of the  $\alpha$  phase was investigated primarily with light metallography. In some specimens TEM was necessary to determine if a phase transformation had taken place. TEM was used also to identify the precipitates observed with LM and to determine their orientation relationships with the matrix. XRD measurements were performed to verify the composition dependence of the  $\beta$  phase lattice parameter.

Before presenting the results of this investigation, it should be noted that there is a fundamental difficulty in determining the  $\beta$ transus in this alloy system. To illustrate this, the diffusion data of Figures 4.3 and 4.4 have been superimposed on the phase diagram



FIGURE 4.9 Alloys'and aging temperatures used in the present study

calculations of Figure 4.8 in Figure 4.10. To effect the highest possible diffusivity in a given alloy, it is necessary to age it at a temperature very near the  $\beta$  transus. If equilibrium could be achieved, a low  $\alpha$  phase volume fraction would be the result. Increasing the niobium content of an alloy aged at a given temperature decreases the volume fraction of a precipitated not only because the alloy is closer to the  $\beta$  transus, but also because the precipitation kinetics are reduced due to the compositional dependence of the diffusivity. In addition, it should be noted that aging high niobium alloys well within the two-phase region may not result in precipitation because of the small diffusion coefficients. For these extremely difficult to make an experimental reasons, it is determination of the  $\beta$  transus.

#### 4.5.1 Microstructures Near the $\beta$ Transus

An example of the nature of the precipitation observed is shown in Figure 4.11. This is a light micrograph of a 30% Nb specimen aged for 960 hours at 500C. This micrograph shows two  $\beta$  phase grains, the intervening grain boundary, and dense  $\alpha$  phase precipitation. The 1000C recrystallization heat treatment appeared to effect complete recovery in the upper grain, while lattice defects were still present in the lower grain.

A needle-shaped a precipitate morphology was observed in all specimens. The a precipitates never assumed an equiaxed morphology.



FIGURE 4.10 Superposition of the phase diagram calculations and the niobium diffusion coefficients



FIGURE 4.11 Light micrograph of the 30-960/500 specimen showing  $\alpha$  phase precipitation

The aspect ratio of the needles decreased as the diffusion coefficient was decreased, either by increasing the niobium content of an alloy, or by aging it at a lower temperature. In those specimens in which the individual precipitates were too small to be resolved with LM, TEM demonstrated that they were still needle-shaped.

The  $\alpha$  needles were found to be aligned with specific directions in the  $\beta$  matrix. This is quite noticeable at the boundaries shown in Figure 4.11. TEM showed that the long axes of the needles were parallel to the <113> $\beta$  directions, not the <110> directions as noted by Williams (WIL73) (see section 3.6.6). The  $\alpha$  precipitates obeyed the Burger's orientation relationships.

Figure 4.11 shows that heterogeneous nucleation sites are preferred for  $\alpha$  phase precipitation. In addition, the precipitates which nucleated at the grain and sub-grain boundaries are larger and their density lower than those which precipitated in the recrystallized  $\beta$  grains.

The effect of aging time on  $\alpha$  phase precipitation is shown in Figures 4.12a and b. These are micrographs of the 25-96/600 and 25-960/600 specimens, respectively. With continued aging, the size and volume fraction of the precipitates increases, both in the matrix and at the grain boundaries. This effect was observed in the other specimens aged at 600C as well. A slight exception was the 20% Nb specimens aged at 600C in which the individual precipitates had coarsened with increased aging, but, due to the dense precipitation, it could not be determined that the precipitate volume fraction had



FIGURE 4.12 Light micrographs showing the effect of aging time on precipitation in 25% Nb specimens a) 25-96/600, b) 25-960/600 increased. A change in precipitate volume fraction was difficult to observe in specimens aged at lower temperatures for the same reason.

The effect of aging temperature is shown in Figures 4.13a and b. These are micrographs of the 35-960/500 and 35-960/600 specimens, respectively. Increasing the aging temperature results in increased diffusivity, but also brings the specimen closer to the  $\beta$  transus. The net effect is a marked decrease in the precipitate volume fraction concomitant with an increase in the size of the individual precipitates. This effect was observed in the other alloys as well.

Increasing the niobium content of an alloy has a two-fold effect as discussed at the beginning of this section. These effects are shown in Figures 4.14 a - e for specimens aged 960 hours at 600C.

The effect of decreasing diffusivity with increasing niobium content was demonstrated in the alloys aged at 500C as well. According to the phase diagram calculation of Kaufman and Bernstein (KAU70), all alloys of the present investigation were well within the two-phase region at this temperature, thus eliminating complications due to approaching the  $\beta$  transus. Using LM, the decrease in the precipitate volume fraction with increasing niobium content was evident in alloys with compositions up to 40% Nb after aging 960 hours. TEM had to be used to observe the extremely small  $\alpha$ precipitate nuclei in the 50-960/500 specimen.

It is well known that diffusion along dislocations and grain boundaries is more rapid than in the bulk. It has been shown also that heterogeneous nucleation sites are preferred for  $\alpha$  phase



FIGURE 4.13 Light micrographs showing the effect of aging temperature on precipitation in 35% Nb specimens a) 35-960/500, b) 35-960/600



FIGURE 4.14 Light micrographs showing the effect of alloy composition on precipitation a) 20-960/600, b) 25-960/600



FIGURE 4.14 Light micrographs showing the effect of alloy composition on precipitation c) 30-960/600, d) 35-960/600



FIGURE 4.14 Light micrograph showing the effect of alloy composition on precipitation e) 40-960/600

precipitation. The alloy rods of this investigation had been swaged to 3mm, introducing a true strain of ~2. To determine if this slight amount of cold-work would enhance the nucleation and growth of  $\alpha$ precipitates, specimens of the 50, 60 and 70% Nb alloys were aged for 3696 hours (154 days, .42 years) at 500C without the 1000C recrystallization anneal. No  $\alpha$  phase precipitation was observed in these specimens, though some recovery was evident.

Aging at 700C produced small precipitates, which were visible with LM, in the 20 - 40% Nb alloys. The precipitation was confined primarily to the grain boundaries, though there were some matrix precipitates. The extent of precipitation was not greatly affected by aging time. Examples of this are shown in Figures 4.15a and b. These are micrographs of the 25-288/700 and 30-288/700 specimens. The effect of the fast water quench following aging can be seen in the 25% Nb specimen. The  $\beta$  phase in both the 20 and 25% Nb specimens transformed to martensite during the quench from 700C, though the transformation was not uniform in the 25% Nb specimen.

#### 4.5.2 X-Ray Diffraction Results

The XRD specimen preparation technique was discussed in section 2.7. Alloys that had been aged for 288 hours were powdered and then annealed at the aging temperature. The time of the post-filing anneal was 24 hours for alloys aged at 500 and 600C, 3 hours for those aged at 700C.



FIGURE 4.15 Light micrographs showing precipitation after aging at 700C a) 25-288/700, b) 30-288/700

The titanium and niobium used in the fabrication of the alloys of this investigation were filed, annealed and x-rayed also. The niobium powder was annealed for 10 minutes at 800C, the titanium powder, 24 hours at 600C. The lattice parameter of the niobium was  $.33003 \pm .00001$  nm. The titanium diffraction pattern did not contain sharp high angle lines, making a precise determination of its lattice parameters difficult. The parameters that were determined were: a = .2956 nm, c/a = 1.5953.

 $\alpha$  phase reflections were found in the diffraction patterns of the 20 - 40% Nb specimens aged at all three temperatures. Though the diffraction lines were always diffuse, their presence was unambiguous. The intensity of the  $\alpha$  pattern decreased with increasing niobium content. No  $\alpha$  lines were observed in the patterns of the 50 - 70% Nb specimens.

An additional diffraction line was seen in the 20 - 40% Nb specimens aged at 600C. This line had a d-spacing slightly smaller than that of the (101) a line and did not match the d-spacings of any of the reported oxides, nitrides or carbides.

The  $\beta$  phase lattice parameters measured in the present investigation are given in Table 4.8. These data are plotted as a function of composition in Figure 4.16.

As in the data of Hansen, et al. (HAN51), there is a minimum in the lattice parameter at about 30% Nb. To determine if this minimum was real or just due to kinetic limitations, powders of the 20 and 30%

## TABLE 4.8

## $\boldsymbol{\beta}$ Phase Lattice Parameters

#### . 288/700

<u>% Nb</u>	a (nm)
20	.32821 + .00002
25	•32832 <del>+</del> •00002
30	.32829 <del>+</del> .00006
35	.32843 <del>+</del> .00002
40	•32846 <del>+</del> •00002
50	-
60	.32880 + .00003
70	• 32909 <u>+</u> • 00002

## 288/600

<u>% Nb</u>	a (nm)
• •	
20	$.32827 \pm .00001$
25	.32828 + .00004
30	$.32823 \pm .00002$
35	•32836 <del>+</del> •00003
40	•32843 <del>+</del> •00004
50	•32856 <del>+</del> •00003
60	.32879 + .00002
70	.32915 + .00002

# 288/500

<u>% Nb</u>	a (nm)
20	<b>.</b> 32838 + <b>.</b> 00005
25	.32834 + .00002
30	.32831 + .00002
35	• <b>3</b> 2834 + • • 00003
40	• <b>3</b> 2842 + • • 00004
50	.32854 + .00007
60	•32878 <del>+</del> •00009
70	-

.



FIGURE 4.16 ß phase lattice parameters measured in this study (data given in Table 4.8)

<u>% Nb</u>	<u>T (C)</u>	<u>t (h)</u>	a (nm)
20	500	96 288 960	.32833 + .00004 .32838 + .00005 .32834 + .00002
30	500	96 288 960	$\begin{array}{r} .32837 + .00005 \\ .32831 + .00002 \\ .32830 + .00005 \end{array}$
20	600	96 288 960	.32823 + .00003 .32827 + .00001 .32828 + .00002
30	600	96 288 960	.32834 + .00003 .32823 + .00002 .32829 + .00001

.

.

## TABLE 4.9

÷

•

Effect of Aging Time on the  $\beta$  Phase Lattice Parameters

Nb alloys aged for 96 and 960 hours at 500 and 600C were x-rayed. The results from these specimens are given in Table 4.9.

#### 4.6 Discussion of the Results

The micrographs of Figures 4.12 - 4.15 indicate that equilibrium is very difficult to establish in this alloy system. It was noted in section 4.5.1 that the 20% Nb specimens aged at 600C may have had a constant  $\alpha$  phase volume fraction. If it is assumed that this alloy reaches equilibrium after 960 hours, the time required to reach equilibrium in the other alloys can be estimated using the diffusion data of section 4.2.4. These estimates are given in Table 4.10. (Note that the aging times are in <u>years</u> (365 days -- no leap years).) These show quite clearly the impossibility of achieving equilibrium in the high niobium alloys. This was confirmed in the specimens aged for .42 years at 500C.

The specimens aged at 600C appeared to be in the two-phase region. With the exception of the 30% Nb specimen, the volume fraction of  $\alpha$  precipitation decreased with increasing niobium content in accordance with the effects discussed in section 4.5. It will be recalled that the 30% Nb alloy had the highest oxygen content of any of the alloys and that interstitial oxygen stabilizes the  $\alpha$  phase. For these reasons, it is believed that the high volume fraction of  $\alpha$ precipitation observed in this alloy may have been due to interstitial oxygen.

## TABLE 4.10

## Estimated Times to Reach Equilibrium at 600C Based on 20-960/600

<u>% Nb</u>	t (yrs)
20	.1
25	• 5
30	2.1
35	9.4
40	41
50	800

Aging at 700C produced very small precipitates with a very low volume fraction. As in the 30-960/600 specimen, the precipitate volume fraction in the 30-288/700 specimen was greater than in the other specimens. It is believed for all specimens aged at 700C, that interstitial impurities were the cause of the observed precipitation and that alloys aged at this temperature should be single-phase.

With this interpretation, the results of the present study are in good agreement with those of Hansen, et al. (HAN51), Imgram, et al. (IMG61) and Ronami, et al. (RON70). The present study has demonstrated that substantial aging times are required to establish equilibrium in this alloy system, corroborating the assumption that kinetic limitations affected the  $\beta$  transus determination of Brown, et al. (BR064, BR066). The results of the present study also show that the calculation of Murray (MUR84) does not represent the actual phase diagram.

On the basis of the present data, a new phase diagram may be calculated. This is shown in Figure 4.17. The lattice stability parameters of Kaufman and Bernstein (KAU70) were used in these calculations. The  $\alpha$  phase interaction parameter used was 3050 cal/mole; the  $\beta$  phase interaction parameter was 3500 cal/mole. The  $\beta$  transus of this calculation is in good agreement with the experimental data. This calculation also predicts a small, but stable  $\beta$  phase miscibility gap.

The calculation of the  $\alpha$  transus, however, is not in agreement with the data of that boundary. The fit of the calculation to the



FIGURE 4.17a Comparison of experimental phase diagram data with the proposed calculation



⊼ ℃

FIGURE 4.17b The proposed phase diagram calculation

data could be improved by increasing the  $\alpha$  phase interaction parameter; however, doing so would necessitate increasing the  $\beta$  phase interaction parameter in order to maintain the fit of the  $\beta$  transus. This would result in an even larger stable  $\beta$  phase miscibility gap. This phase diagram calculation indicates that yet more data are required.

The β phase lattice parameter of alloys with compositions between 50 and 100% Nb was found to vary linearly with niobium content. A least squares fit of the data yielded:

### a = .32702 + .00003x nm

where x is the atomic fraction of niobium. In this range of compositions, Hansen's data (HAN51) fall ~.15pm below those of the present study. This difference may be due to different impurity contents of the alloys or powders. The data of Hickman (HIC69a) and Rudy, et al. (RUD69) are ~.3pm above those of the present study in the same composition range, most likely for the same reason.

Below 40% Nb there was little variation of the lattice parameter with alloy composition. This is indicative of aging in a two-phase field, which was reinforced by the presence of  $\alpha$  reflections in the diffraction patterns. The lattice parameter of the specimens aged at 700C, however, also showed little variation with alloy composition, even though these specimens should have been aged in a single-phase region. It would not be expected that the slight precipitation caused by the impurities in these specimens would have affected the lattice parameter, leaving the cause of this effect still uncertain.

The data of Table 4.9 demonstrate two points. First, the minimum in the lattice parameter observed at 30% Nb appears to be a real effect. Within the precision of the Debye-Scherrer technique, the lattice parameters of the aged 20 and 30% Nb specimens were unaffected by increasing the aging time. A monotonic lattice parameter increase would have been expected in the event of niobium enrichment of the matrix due to  $\alpha$  phase precipitation. The time estimates of Table 4.10 indicate, however, that aging for 960 hours may have been insufficient to produce the expected changes.

The second point illustrated by the data of Table 4.9 is the difference between precision and accuracy. The errors quoted in Tables 4.8 and 4.9 are those arising from the Nelson-Riley extrapolation. The lattice parameter differences observed in this study were very close to the lattice parameter variations measured by Hickman (HIC69a) in his attempt to determine the composition of the isothermal  $\omega$  phase (see section 3.3.4). While Hickman believed the observed variations were real because of the precision of the x-ray technique used, the results of this study indicate that they were probably due to variations in specimen preparation. In addition, the lattice parameters measured by Hickman for the high niobium alloys are much higher than those of Hansen, et al. (HAN51) and of the present study. Again, these data show that precision does not imply accuracy.

#### 4.7 Summary

This investigation of the  $\beta$  transus has demonstrated several points to which the literature has alluded. The first is that equilibrium in this alloy system is practicably impossible to achieve due to the exponential drop of the diffusion coefficient with increasing niobium content. At low aging temperatures, the compositional dependence of diffusivity creates a kinetically limited β transus, instead of the desired thermodynamic transus. At high aging temperatures, the diffusivity effect is combined with the effect of aging near the  $\beta$  transus, resulting in a broad, uncertain boundary, instead of a sharp one. These two effects are further compounded by the effects of interstitials.

Despite these difficulties, the results of the present study corroborate the data of Hansen, et al. (HAN51), Imgram, et al. (IMG61) and Ronami, et al. (RON70). These results show that the data of Brown, et al. (BR064, BR066) were affected by kinetic difficulties and that phase diagram calculations based on them are not representative of the true nature of the phase diagram. A new phase diagram has been calculated which is in good agreement with the experimental  $\beta$  transus.

Measurements of the  $\beta$  phase lattice parameter confirm its dependence on alloy composition. The lattice parameter decreases linearly with decreasing niobium content between 100 and 50% Nb. For alloys with niobium compositions less than 50%, there is little variation with composition, regardless of heat treatment temperature.

CHAPTER FIVE

## FUTURE WORK AND FINAL SUMMARY

#### CHAPTER FIVE

#### FUTURE WORK and FINAL SUMMARY

The results of the present study have shown that there are several aspects of the phase transformations in Ti-Nb alloys that are deserving of further investigation. Most of these are concerned with the metastable equilibria. What follows is a discussion of a few of the more interesting prospects.

It has been shown repeatedly that decreasing the niobium content of an alloy increases the variability of its microstructure. The lowest niobium content of the alloys of the present study was 20%. It would be interesting to repeat the quenching, and quenching and aging experiments on alloys of 10 and 15% Nb.

The effects of microstructure on resistivity were demonstrated in this study. The results of this study, however, did not really permit the separation of the effects on resistivity due solely to composition from those due solely to  $\omega$  phase precipitation. The results were correlated with the change of  $\omega$  phase precipitation from "virtual" to "real", but this includes a compositional effect as well. In order to separate the two effects, it is necessary to produce Ti-Nb alloys which are truly single-phase. A measurement of the resistivity of  $\beta$ -Ti at room temperature and below also would be of value in determining the compositional dependence of  $\rho$ . Extrapolation of the resistivity of  $\beta$ -Ti from above 882C indicates that at room temperature,  $\beta$ -Ti has a resistivity of ~130µ $\Omega$ -cm, which is very high for a pure metallic element. This value, however, is in accord with the extrapolated resistivity data of the present study.

The supposition that the process of  $\omega$  phase structure refinement continues below room temperature and that this alone results in a negative  $\partial \rho / \partial T$  in certain alloys is need of verification. The interpretation of this study suggests that from the temperature at which the collapse of the  $(111)\beta$  planes begins,  $3\rho/3T$  of an alloy decreases with decreasing temperature. Under the proper conditions, it may even become negative in a certain range of temperatures. After the w precipitation process has produced a stabilized microstructure, θρ/θT would become positive and remain constant with decreasing temperature. Measurements of  $\rho$  during the quench from 1000C would indicate the temperatures at which these events occur. In the 20 and 25-AC specimens, the temperature at which precipitation of the  $\omega$  phase begins is apparently above room temperature. The temperature at which this process ends is ~80K. In the other specimens of this study, both temperatures appear to be above room temperature.

The kinetics of isothermal  $\omega$  phase precipitation are in need of further study. The results of this study were unusual in their own right, and were not in agreement with either of the other studies.

The effects of quenching prior to isothermal aging may be studied in more detail. Specimens could be quenched to some temperature above room temperature, held for 15 minutes, and then aged at an elevated temperature in order to determine if there is a temperature to which quenching before aging no longer produces  $\omega$  precipitates.

This study has shown that equilibrium in the high niobium alloys is practicably impossible to achieve in recrystallized alloys. The minimal amount of cold-work given the alloys of this study was insufficient to produce any effect. Based on the work of others in the Superconducting Materials Research Group here, aging specimens containing the severe cold-work typical of superconductor wire may yield interesting results.

5.1 Final Summary

A fundamental study of the phase transformations which occur in the Ti-Nb binary alloy system has been completed. Eight alloys in the range 20 to 70% Nb were investigated using TEM, LM and XRD. Measurements of electrical resistivity and Vicker's microhardness also were performed. Emphasis was placed on the minimization of interstitial contamination in all steps of alloy fabrication and specimen preparation. In order to eliminate the effects of prior cold-working, the alloys studied were recrystallized at 1000C. Phase transformations were studied in alloys which had been quenched to room temperature after recrystallization, quenched to room temperature and then isothermally aged, and in those which had been isothermally aged without a prior room temperature quench.

It was found that the microstructures of the quenched 20 and 25% Nb alloys were extremely sensitive to quench rate -- with a fast quench producing martensite, a slow quench, the  $\omega$  phase. The microstructures of the higher niobium content alloys were much less sensitive to quench rate.

The microstructures of the isothermally aged 20 and 25% Nb alloys were found to be sensitive to prior thermal history. Alloys quenched room temperature and then aged at 400C contained large  $\boldsymbol{\omega}$ to while those aged without precipitates. an intermediate room temperature quench contained a precipitates. Isothermal  $\omega$  phase precipitation was found in quenched 20 and 25% Nb specimens aged at 300, 350 and 400C. The 35% Nb alloys aged between 300 and 500C contained precipitates which could not be identified using electron diffraction, but were determined to be nuclei of the a phase.

Aging at 450, 500 and 600C produced  $\alpha$  precipitates in the 20 to 40% Nb alloys. The  $\beta$  transus in this system could not be determined unambiguously. A phase diagram was calculated which fit the experimental data, but also predicted a small, but stable,  $\beta$  phase miscibility gap.

BIBLIOGRAPHY

#### BIBLIOGRAPHY

- [ABL77] Ablitzer, D., Phil Mag, 35(5), 1239-1256 (1977)
- [AF073] Afonikova, N.S., Degtyareva, V.F., Litvin, Yu.A., Rabin kin, A.G. and Skakov, Yu.A., Sov Phys-Sol St, 15(4), 746-749 (1973)
- [AHL78] Ahlberg,L.A., Buck,O. and Paton,N.E., Scripta Met, <u>12</u>, 1051-1054 (1978)
- [AME54] Ames, S.L. and McQuillan, A.D., Acta Met, 2, 831-836 (1954)
- [AND59] Andersson, S., Acta Chem Scand, 13, 415-419 (1959)
- [ASK65] Askill, J. and Gibbs, G.B., Phys Stat Sol, 11, 557-565 (1965)
- [BAG58] Bagariatskii, Iu.A., Nosova, G.I. and Tagunova, T.V., Sov Phys-Doklady, <u>3</u>, 1014-1018 (1958)
- [BAK69] Baker, C. and Sutton, J., Phil Mag, 19, 1223-1255 (1969)
- [BAL72] Balcerzak, A.T. and Sass, S.L., Met Trans, 3, 1601-1605 (1972)
- [BAR66] Barrett, C. and Massalski, T.B., Structure of Metals, McGraw-Hill, New York (1966)
- [BER63] Berlincourt, T.G. and Hake, R.R., Phys Rev, <u>131</u>(1), 140-157 (1963)
- [BON60] Bond, W.L., Acta Cryst, 13, 814-850 (1960)
- [BR064] Brown, A.R.G., Clark, D., Eastabrook, J. and Jepson, K.S., Nature, 210, 914-915 (1964)
- [BR066] Brown,A.R.G. and Jepson,K.S., Mem Sci Rev Met, <u>63</u>(6), 575-584 (1966)
- [BUN65] Bundy, F.P., ASTM Spec Tech Pub #374, 52-67 (1965)
- [CHA74] Chandrasekaran, V., Taggart, R. and Polonis, D.H., J Mat Sci, 9, 961-968 (1974)
- [CHA76] Chang, A.L.J., Sass, S.L. and Krakow, W., Acta Met, <u>24</u>, 29-36 (1976)
- [COL74] Collings, E.W., Phys Rev B, 9(10), 3989-3999 (1974)

- [COL78] Collings, E.W., Electrical Transport and Optical Properties of Inhomogeneous Media, ed. by Garland, J.C. and Tanner, D.B., AIP Conf Proc #40, New York (1978)
- [COL84] Collings, E.W., The Physical Metallurgy of Titanium Alloys, ASM, Metals Park, OH (1984)
- [CO069] Cook, H.E. and deFontaine, D., Acta Met, 17, 915-924 (1969)
- [DAV79] Davis, R., Flower, H.M. and West, D.R.F., J Mat Sci, <u>14</u>, 712-722 (1979)
- [DAV79a] Davis, R., Flower, H.M. and West, D.R.F., Acta Met, <u>29</u>, 1041-1052 (1979)
- [DEF70] deFontaine, D., Acta Met, 18, 275-279 (1970)
- [DEF71] deFontaine, D., Paton, N.E. and Williams, J.C., Acta Met, <u>19</u>, 1153-1162 (1971)
- [DUW51] Duwez, P., J Metals, 765-771 (1951)
- [DUW53] Duwez, P., Trans ASM, 45, 934-940 (1953)
- [DYA83] D'yakonova, N.B., Lyasotskii, I.V., Zaitsez, A.I. and Luzanov, V.V., Sov Phys-Sol St, 25(7), 1194-1198 (1983)
- [EIN78] Einziger, R.E., Mundy, J.N. and Hoff, H.A., J Nuc Mat, <u>69-70</u>, 523-525 (1978)
- [FAT83] Fatemi, M., Pande, C.S. and Child, H.R., Phil Mag A, <u>48</u>(4), 479-500 (1983)
- [FL082] Flower, H.M., Davis, R. and West, D.R.F., <u>Titanium and Titanium</u> <u>Alloys: Scientific and Technological Aspects</u>, <u>3</u>, 1703-1715, Plenum Press, New York (1982)
- [FR076] Fromm, E. and Gebhardt, E., <u>Gase und Kohlenstoff in Metallen</u>, Springer-Verlag, Berlin (1976)
- [FR080] Froes,F.H., Yolton,C.F., Capenos,J.M., Wells,M.G.H. and Williams,J.C., Met Trans A, <u>11A(1)</u>, 21-31 (1980)
- [GIB63] Gibbs,G.B., Graham,D. and Tomlin,D.H., Phil Mag, <u>8</u>, 1269-1282 (1963)
- [GUI76] Guiles, N.L. and Ono, K., Effect of Hydrogen on the Behavior of Materials, ed. by Thompson, A.W. and Bernstein, I.M., 666-675, TMS-AIME, Warrendale, PA (1976)
- [GUS82] Guseva,L.N. and Dolinskaya,L.K., Titanium and Titanium Alloys: Scientific and Technical Aspects, ed. Williams,J.C. and Belov,A.F., 1559-1565, Plenum Press, New York (1982)
- [GUZ66] Guzei,L.S., Sokolovzkaya,E.M. and Grigor'ev,A.T., J Moscow Univ Chem, 21(5), 406-409 (1966)
- [HAM72] Hammond, C., Scripta Met, 6, 569-570 (1972)
- [HAN51] Hansen, M., Kamen, E.L., Kessler, H.D. and McPherson, D.J., J Metals, 3, 881-888 (1951)
- [HAN58] Hansen, M. and Anderko, K., Constitution of Binary Alloys, Second Edition, McGraw Hill, New York (1958)
- [HAN85] Hanada,S., Ozeki,M. and Izumi,O., Met Trans A, <u>16A(5)</u>, 789-795 (1985)
- [HAW81] Hawksworth, D.G., PhD Thesis, University of Wisconsin-Madison (1981)
- [HAT68] Hatt, B.A. and Rivlin, V.G., Brit J App Phys, 1(2), 1145-1149 (1968)
- [HAY85] Hayman, C. and Gerberich, W.W., Met Trans A, <u>16A(2)</u>, 187-195 (1985)
- [HIG69] Hickman, B.S., J Mat Sci, 4, 554-563, (1969)
- [HIC69a] Hickman, B.S., Trans TMS AIME, 245, 1329-1335 (1969)
- [H072] Ho,J.C. and Collings,E.W., Phys Rev B, <u>6</u>(10), 3727-3738 (1972)
- [HOC82] Hochstuhl, P. and Obst, B., J de Physique, <u>43</u>(12), 133-138 (1982)
- [IMG61] Imgram, A.G., Williams, D.N., Wood, R.A, Ogden, H.R. and Jaffee, R.I., WADC Tech Report 59-595, Part II (1961)
- [JEP70] Jepson, K.S., Brown, A.R.G. and Gray, J.A., <u>The Science</u>, <u>Technology and Application of Titanium</u>, ed. by Jaffee, R.I. and Promisel, N.E., 677-690, Pergamon Press (1970)
- [KAN63] Kaneko, H. and Huang, Y.C., Nippon Kinzoku Gakkai, <u>27(8)</u> 387-393 (1963)

- [KAU70] Kaufman,L. and Bernstein,H., Computer Calculations of Phase Diagrams, Academic Press, New York (1970)
- [KHA81] Khaled, T., Narayanan, G.H. and Copley, S.M., Met Trans A, 12A(2), 293-298 (1981)
- [KRA67] Kramer, D. and Rhodes, C.G., Trans TMS AIME, 236, 1612-1615 (1967)
- [LAR80] Larbalestier, D.C., Adv Cryo Eng, <u>26</u>, ed. by Clark, A.F. and Reed, R.P., 10-36, Plenum Press, New York (1980)
- [LIB63] Libanati, C.M. and Dyment, F., Acta Met, 11, 1263-1268 (1963)
- [LUN65] Lundy, T.S., Winslow, F.R., Pawel, R.E. and McHargue, C.J., Trans TMS AIME, 233, 1533-1539 (1965)
- [LY081] Lyon, O., J Less-Common Met, 81, 103-113 (1981)
- [LY083] Lyon, O., Severac, C. and Servant, C., Phil Mag A, <u>48(5)</u>, 825-839 (1983)
- [MCC71] McCabe, K.K. and Sass, S.L., Phil Mag, 23, 957-970 (1971)
- [MEH71] Mehrer, H., Kunz, P. and Seeger, A., Defects in Refractory Metals: Proceedings of the International Discussion Meeting, ed. by deBatist, R., Nittoul, J. and Stals, L. (1971)
- [MOF82] Moffat, D.L., Preliminary Examination, University of Wisconsin-Madison (1982)
- [MOR73] Morniroli, J.P. and Gantois, M., Mem Sci Rev Met, 70(11), 831-842 (1973)
- [MUR81] Murray, J.L., Bull Alloy Phase Diagrams, 2(1), 55-61 (1981)
- [MUR84] Murray, J.L., To be Published
- [PAT73] Paton, N.E. and Williams, J.C., Scripta Met, 7, 647-650 (1973)
- [PAT75] Paton, N.E., Buck, N.E. and Williams, J.C., Scripta Met, 9, 687-691 (1975)
- [PAT76] Paton, N.E. and Buck, O., Effect of Hydrogen on the Behavior of Materials, ed. by Thompson, A.W. and Bernstein, I.M., 83-90, TMS-AIME, Warrendale, PA (1976)
- [PEA62] Peart, R.F. and Tomlin, D.H., Acta Met, 10, 123-134 (1962)

- [PEA62a] Peart, R.F., Graham, D. and Tomlin, D.H., Acta Met, <u>10</u>, 519-523 (1962)
- [PON79] Pontau, A.E. and Lazarus, D., Phys Rev B, <u>19</u>(8), 4027-4037 (1979)
- [PRE75] Prekul, A.F., Rassokhin, V.A. and Volkenshtein, N.V., Sov Phys JETP, 40(6), 1134-1136 (1975)
- [RES60] Resnick, R. and Castleman, L.S., Trans TMS AIME, <u>218</u>, 307-310 (1960)
- [RON70] Ronami,G.N., Kuznetsova,S.M., Fedotov,S.G. and Konstantinov,K.M., Moscow Univ Phys Bull, 25(2), 55-57 (1970)
- [ROU70] Roux, F. and Vignes, A., Rev de Phys App, 5, 393-405 (1970)
- [RUD69] Rudy, E., Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems, Part V: Compendium of Phase Diagram Data, AFML-TR-65-2, Part V (1969)
- [SAS69] Sass, S.L., Acta Met, 17(7), 813-820 (1969)
- [SAS72] Sass, S.L., J Less-Common Met, 28, 157-173 (1972)
- [SAT60] Sato, T., Hukai, S. and Huang, Y-C, J Australian Inst Met, <u>5</u>(2), 149-153 (1960)
- [SHU69] Shunk, F.A., Constitution of Binary Alloys, Second Supplement, McGraw Hill, New York (1969)
- [SIL58] Silcock, J.M., Acta Met, 6, 481-493 (1958)
- [SIL70] Silcock, J.M., The Science, Technology and Application of <u>Titanium</u>, ed. by Jaffee, R.I. and Promisel, N.E., 731-732, Pergamon Press (1970)
- [VOH78] Vohra, Y.K., J Nuc Mat, 75, 288-293 (1978)
- [VOZ70] Vozilkin,V.A., Buynov,N.N., Bychkov,Yu.F., Vereshchagin,V.G., Karasik,V.R., Kurganov,G.B. and Mal'tsev,V.A., Phys Met Metallog, 30(4), 82-90 (1970)
- [WAL68] Walsoe deReca, N.E. and Libanati, C.M., Acta Met, <u>16</u>, 1297-1305 (1968)
- [WIL73] Williams, J.C., <u>Titanium Science and Technology</u>, <u>3</u>, ed. by Jaffee, R.I. and Burke, H.M., 1433-1494, Plenum Press, New York (1973)

APPENDIX A

# SELECTED AREA DIFFRACTION PATTERN CALCULATIONS

#### APPENDIX A

## SELECTED AREA DIFFRACTION PATTERN CALCULATIONS

Phase identification is often based on SAD patterns obtained in an electron microscope. The SAD patterns of  $\alpha$ ,  $\omega$  and  $\alpha$ " are similar, yet posses important differences. SAD patterns for these three structures are shown superimposed on a (110) $\beta$  pattern, which was the matrix pattern most frequently observed during the course of this investigation. The SAD pattern for the second phase orientation which gives the most reflections in a (110) $\beta$  pattern will be the only one shown for each example. The key to these SAD patterns is:

- matrix reflection
- second phase reflection
- + double diffraction reflection

In the  $\beta + \alpha$  and  $\beta + \alpha''$  patterns, double diffraction from the matrix reflections produces several extra reflections. This is the only effect considered for these microstructures. In the  $\beta + \omega$  pattern, double diffraction from the matrix reflections does not produce any extra reflections, nor does double diffraction from  $\omega$  reflections of the same variant. However, extra reflections do occur when the pattern of one of the  $\omega$  variants is doubly diffracted from a reflection of one of the other  $\omega$  variants.



а

Ь

с

FIGURE A.1 The  $(110)\beta + (001)\alpha''$  SAD pattern  $a\beta = .3280nm, a\alpha'' = .3135nm, b/a = 1.552, c/a = 1.489$ a)  $(010)\alpha'' || (\overline{9}91)\beta$ b)  $(010)\alpha'' || (\overline{9}91)\beta + (010)\alpha'' || (9\overline{9}1)\beta$ c) Double diffraction effects included

.



a

Ь

с

FIGURE A.2 The  $(110)\beta$  +  $(11\overline{2}0)\omega$  SAD pattern  $a\beta = .3280nm$ ,  $a\omega = .4639nm$ , c/a = .6123a)  $(0001)\omega$  ||  $(\overline{1}11)\beta$ b)  $(0001)\omega$  ||  $(\overline{1}11)\beta$  +  $(0001)\omega$  ||  $(1\overline{1}1)\beta$ c) Double diffraction effects included



а

Ъ

с

FIGURE A.3 The  $(110)\beta$  +  $(0001)\alpha$  SAD pattern  $a_{\beta} = .3280$ nm,  $a_{\alpha} = .297$ nm, c/a = 1.5825a)  $(\overline{1210})\alpha || (\overline{111})\beta$ b)  $(\overline{1210})\alpha || (\overline{111})\beta + (\overline{1210})\alpha || (1\overline{11})\beta$ c) Double diffraction effects included

APPENDIX B

ELECTRON AND X-RAY DIFFRACTION RELATIVE INTENSITY CALCULATIONS

2

ŧ.,

## TABLE B.1

Relative Intensity Calculations for the  $\beta$  Phase

HKL	<u>d (nm)</u>	<u>2</u>	Ix	Ie
110	.23214	38.75	100.00	100.00
200	.16415	55.97	14.33	44.67
211	.13403	70.15	25.74	24.69
220	.11607	83.15	7.49	15.25
310	.10382	95.79	10.74	10.14
222	.09477	108.72	3.07	7.13
321	.08774	122.76	18.53	5.22
400	.08208	139.58	2.84	3.95
330	.07738	168.96	18.74	3.05
411	.07738	168.96	37.48	3.05

Alloy Composition: 30% Nb, Temperature: 300K a = .3283nm Angles for Cu Kαl

ΤÆ	₹B	L	E	В	•	2

.

Relative Intensity Calculations for the  $\alpha$  Phase

HKL	<u>d (nm)</u>	<u>2                                    </u>	Ix	Ie
100	.25721	34.85	25.86	30.06
002	.23500	38.26	25.55	100.00
101	.22563	39.92	100.00	68.72
102	.17349	52.71	12.64	12.04
110	.14850	62.49	13.55	30.53
103	.13380	70.29	13.28	16.30
200	.12860	73.58	1.89	4.74
112	.12554	75.69	13.70	17.40
201	.12404	76.77	9.81	12.51
004	.11750	81.92	1.77	13.67
202	.11282	86.11	2.30	2.93
104	.10688	92.22	1.93	2.38
203	.09940	101.58	4.81	5.33
120	.09722	104.80	1.54	1.62
211	.09520	108.01	8 <b>9</b> 4	4.46
114	.09214	113.42	5.77	5.18
212	.08983	118.05	2.86	1.16
105	.08829	121.47	4.32	3.24
204	.08675	125.22	1.46	1.00
300	.08574	127.89	2.98	3.80
213	.08260	137.63	9.97	2.41
302	.08054	145.99	7.79	2.86

Alloy Composition: 5% Nb, Temperature: 300K a = .297nm, c/a = 1.5825 Angles for Cu Kal

\$

#### HKL d (nm) 2Θ IxIe 001 .28430 31.44 7.07 16.37 38.75 110 .23215 100.00 100.00 38.76 88.87 44.44 101 .23214 .17982 111 50.72 8.93 6.19 55.97 25.15 201 .16415 19.46 002 .14215 65.62 5.32 28.75 121 .13403 70.15 22.40 10.60 70.15 300 .13403 12.60 23.85 301 78.89 1.90 1.89 .12123 78.89 112 .12123 17.06 16.99 220 14.55 .11607 83.14 7.29 221 .10746 91.57 1.26 1.22 131 .10382 95.78 9.20 4.26 302 .09752 104.34 9.11 7.51 003 108.73 0.74 .09477 0.16 401 .09477 108.72 3.90 2.98 113.24 3.83 2.67 103 .09224 5.40 222 .08991 117.89 8.60 140 .08774 122.76 8.75 4.88 231 .08774 122.76 7.77 2.17 122.77 0.54 113 .08774 0.97 203 .08572 127.93 4.03 1.96 141 133.46 D.45 .08384 2.14 123 .08041 146.60 10.94 1.49 330 168.92 17.26 2.81 .07738 051 .07738 168.93 15.35 1.25 303 .07738 168.99 3.86 0.31 Alloy Composition: 20% Nb, Temperature: 300K a = .4643nm, c/a = .6123

#### TABLE B.3

Relative Intensity Calculations for the  $\omega$  Phase

Angles for Cu Kal

# TABLE B.4

,

.

Relative Intensity Calculations for the  $\alpha^{\prime\prime}$  Phase

HKL	d (nm)	<u>2</u> <del>0</del>	Ix	Ie
110	.26353	33.99	8.28	12.11
020	.24327	36.92	21.96	71.16
002	.23340	38.54	29.25	100.00
111	.22949	39.22	100.00	87.35
021	.21574	41.83	15.46	29.25
112	.17473	52.31	3.95	4.89
022	.16842	54.43	11.76	30.40
200	.15675	58.86	6.78	38.05
130	.14405	64.65	6.33	19.39
131	.13764	68.05	5.57	8.88
113	.13399	70.18	13.08	21.31
220	.13177	71.54	4.43	14.60
023	.13108	71.97	2.29	7.57
202	.13013	72.58	6.44	21.40
221	.12681	74.80	4.02	6.78
132	.12258	77.85	6.69	11.43
040	.12164	78.57	0.24	1.62
041	.11771	81.74	3.98	13.69
004	.11670	82.60	2.13	14.68
222	<b>.</b> 11474	84.33	5.27	9.04
042	.10787	91.13	0.32	1.05
114	.10671	92.41	0.61	1.01
133	.10571	93.55	2.15	3.51
024	.10522	94.11	2.01	6.54
310	.10217	97.85	0.27	0.85
223	.10056	99.99	1.91	2.90
311	.09981	101.01	4.93	7.36
240	.09610	106.55	0.24	0.67
043	.09583	106.98	2.31	6.26
241	.09412	109.83	4.54	5.83
204	.09361	110.74	2.50	6.30
312	.09360	110.76	0.48	0.60
150	.09294	111.94	2.48	6.12
134	•09068	116.30	3.23	3.62
242	•08886	120.17	0.47	0.49
115	.08800	122.15	4.53	4.42
330	.08784	122.52	1.64	3.17
224	.08736	123.68	3.31	3.10
025	.08716	124.18	0.88	1.62

.

.

Relative Intensity Calculations for the  $\alpha^{\prime\prime}$  Phase

HKL	d (nm)	<u>2</u> <del>0</del>	Ix	Ie
152	.08634	126.26	5.14	4.51
331	.08633	126.30	1.78	1.56
313	.08540	128.80	4.75	3.89
044	.08421	132.31	0.26	0.39
332	.08221	139.06	3.95	2.39
243	.08176	140.79	5.64	3.22
400	.07837	158.68	2.64	2.95
135	.07834	158.91	3.68	1.02

Alloy Composition: 20% Nb, Temperature: 300K a = .3135nm, b/a = 1.552, c/a = 1.489, y = .2 Angles for Cu Kal

APPENDIX C

# CUBIC STEREOGRAPHIC PROJECTIONS

THE [110] PROJECTION



THE [111] PROJECTION



APPENDIX D

EQUATIONS of the REGULAR SOLUTION MODEL

## APPENDIX D

#### EQUATIONS of the REGULAR SOLUTION MODEL

## D.1 Introduction

In this model, the free energy of the  $\alpha$  phase as a function of composition and temperature is given by:

$$G^{\alpha}[x,T] = (1-x)G^{\alpha}_{A} + xG^{\alpha}_{B} - T\Delta S^{\alpha}_{m} + G^{\alpha}_{xs} \qquad D.1$$

where:

 $G_A^{\alpha}$  = free energy, as a function of temperature, of element A in the  $\alpha$  phase  $G_B^{\alpha}$  = free energy, as a function of temperature, of element B in the  $\alpha$  phase x = atomic fraction of B in the  $\alpha$  phase  $\Delta S_m^{\alpha}$  = entropy of mixing in the  $\alpha$  phase  $G_{XS}^{\alpha}$  = excess free energy of mixing in the  $\alpha$  phase

For an ideal solution:

$$\Delta S_{m}^{\alpha} = -R[x \ln x + (1-x) \ln(1-x)] \qquad D.2$$

$$G_{xs}^{\alpha} = 0 \qquad D.3$$

In the regular solution model,  $\Delta S^\alpha_m$  is given by the above equation, but  $G^\alpha_{xs}$  is given by:

$$G_{xs}^{\alpha} = Ax(1-x)$$
 D.4

where A is the regular solution interaction parameter for the  $\alpha$  phase. The free energies of other phases which may occur in the A-B alloy - system are defined similarly.

# 221

## D.2 Two Phase Equilibrium

Equilibrium between the  $\alpha$  and  $\beta$  phases is expressed as:

$$\overline{G}_{A}^{\alpha} \Big|_{x^{\alpha}} = \overline{G}_{A}^{\beta} \Big|_{x^{\beta}} \qquad D.5$$

$$\overline{G}_{B}^{\alpha}\Big|_{X^{\alpha}} = \overline{G}_{B}^{\beta}\Big|_{X^{\beta}} \qquad D.6$$

where the partial molar free energies of A and B in the  $\alpha$  and  $\beta$  phases are given by:

$$\overline{G}_{A}^{\alpha}\Big|_{x^{\alpha}} = G^{\alpha} - x^{\alpha} (\partial G^{\alpha} / \partial x)_{x^{\alpha}} \qquad D.7$$

$$\overline{G}_{B}^{\alpha}\Big|_{X^{\alpha}} = G^{\alpha} - (1-X^{\alpha})(\partial G^{\alpha}/\partial x)_{X^{\alpha}} \qquad D.8$$

The other partial free energies are defined similarly. Combining equations D.1, D.2, D.4 and D.7 yields:

$$\overline{G}_{A}^{\alpha}\Big|_{x^{\alpha}} = G_{A}^{\alpha} + RTln(1-x^{\alpha}) + A(x^{\alpha})^{2} \qquad D.9$$

$$\overline{G}_{A}^{\beta}\Big|_{x^{\beta}} = G_{A}^{\beta} + RTln(1-x^{\beta}) + B(x^{\beta})^{2} \qquad D.10$$

Equating equations D.9 and D.10:

$$G_A^{\alpha} + RTln(1-x^{\alpha}) + A(x^{\alpha})^2 = G_A^{\beta} + RTln(1-x^{\beta}) + B(x^{\beta})^2$$
 D.11

Rearranging equation D.11 gives:

$$G_{A}^{\alpha} - G_{A}^{\beta} = \Delta G_{A}^{\beta+\alpha} = RTln\left(\frac{(1-x^{\beta})}{(1-x^{\alpha})}\right) + B(x^{\beta})^{2} - A(x^{\alpha})^{2} \qquad D.12$$

The corresponding equation for element B is:

$$\Delta G_{B}^{\beta+\alpha} = RTln\left(\frac{x^{\beta}}{x^{\alpha}}\right) + B(1-x^{\beta})^{2} - A(1-x^{\alpha})^{2} \qquad D.13$$

Simultaneous solution of equations D.12 and D.13 yields the equilibrium compositions of the  $\alpha$  and  $\beta$  phases.

D.3 Xo

At some composition, Xo, the free energies of the  $\alpha$  and  $\beta$  phases must be equal. This is expressed as:

$$G^{\alpha}\Big|_{X_{O}} = G^{\beta}\Big|_{X_{O}}$$
 D.14

Using equation D.1, the following equations result:

$$(1-X_0)\Delta G_A^{\beta+\alpha} + X_0\Delta G_B^{\beta+\alpha} + X_0(1-X_0)(A-B) = 0$$
 D.15

$$Xo = \frac{1}{2} \left( 1 - \frac{\Delta G_{B}^{\beta + \alpha} - \Delta G_{A}^{\beta + \alpha}}{B - A} \right) - \sqrt{\frac{1}{4} \left( 1 - \frac{\Delta G_{B}^{\beta + \alpha} - \Delta G_{A}^{\beta + \alpha}}{B - A} \right)^{2} - \frac{\Delta G_{A}^{\beta + \alpha}}{B - A}} D.16$$

If A = B, then:

$$X_{O} = \frac{\Delta G_{A}^{\beta + \alpha}}{\Delta G_{A}^{\beta + \alpha} - \Delta G_{B}^{\beta + \alpha}} \qquad D.17$$

## D.4 The Miscibility Gap

The limiting compositions,  $x_1$  and  $x_2$ , of a  $\beta$  phase miscibility gap are derived in the following manner:

$$\overline{G}_{A}^{\beta}\Big|_{x_{1}} = \overline{G}_{A}^{\beta}\Big|_{x_{2}} \qquad D.18$$

$$\overline{G}_{B}^{\beta}\Big|_{x_{1}} = \overline{G}_{B}^{\beta}\Big|_{x_{2}} \qquad D.19$$

Equations D.18 and D.19 yield, respectively:

$$RTln(1-x_1) + B(x_1)^2 = RTln(1-x_2) + B(x_2)^2$$
 D.20

$$RTlnx_1 + B(1-x_1)^2 = RTlnx_2 + B(1-x_2)^2$$
 D.21

Subtracting equation D.21 from D.20:

$$RT[ln(1-x_1) - lnx_1] - B(1-2x_1) = RT[ln(1-x_2) - lnx_2] + B(1-2x_2) D.22$$

This equation has a solution if  $x_1 = x_2$  or if both sides are equal to zero. The latter solution yields:

$$\frac{B}{RT} = \frac{\ln(1-x_1) - \ln x_1}{1 - 2x_1}$$
 D.23

Substituting  $x_2 = 1 - x_1$  yields the same equation, thus the miscibility gap is symmetric about x = .5

D.5 The Chemical Spinodal

The limits of the chemical spinodal are the inflection points of the  $\beta$  phase free energy curve. They are given by:

$$\frac{\partial^2 G^{\beta}}{\partial x^2} = 0 \qquad D.24$$

$$\frac{RT}{2B} = x(1-x) \qquad D.25$$