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## PHASE EQUILIBRIA IN A T1-6WT%A1-2WT%Nb-1WT%Ta-1WT%Mo ALLOY: MORPHOLOGY, CRYSTAL STRUCTURE AND SOLUTE PARTITIONING

By

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A DISSERTATION

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# DOCTOR OF PHILOSOPHY IN METALLURGICAL ENGINEERING

Department of Mechanics, Metallurgy and Materials Science

#### ABSTRACT

## PHASE EQUILIBRIA IN A T1-6WT%A1-2WT%Nb-1WT%Ta-1WT%Mo ALLOY: MORPHOLOGY, CRYSTAL STRUCTURE AND SOLUTE PARTITIONING

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The objective of this investigation was to establish the crystallographic and morphological aspects of various phases in a Ti-6wt%Al-2wt%Nb-lwt%Ta-lwt%Mo alloy (henceforth called Ti-6211) as a function of thermal history. Various equilibrium and metastable phases can exist in such an alloy depending on the isothermal holding time and temperature in the two-phase or single phase region. The crystal structure and morphology can also be modified by the cooling rate and/or quenching. The high-temperature equilibrium  $\beta$ -phase can either be retained on rapid quenching or it can transform to two possible martensitic phases,  $\alpha'$  and  $\alpha''$ ; where the  $\alpha'$  is a hcp unit cell and the  $\alpha$ " is orthorhombic. Whether the  $\beta$ -phase is retained or the  $\alpha'$ or the  $\alpha$ " martensites form, depends on the solute supersaturation of the equilibrium  $\beta$ -phase. In fact the solute supersaturation of the  $\beta$ -phase suppresses the martensitic start temperature,  $M_e$ , and martensitic final temperature,  $\rm M_{f}$  and if the  $\rm M_{s}$  and/or  $\rm M_{f}$  are below room-temperature then retained  $\beta$  is obtained.

As-received Ti-6211 alloy samples were equilibriated at  $1025^{\circ}C$  (100%  $\beta$ -phase) in an argon atmosphere, down quenched to  $900^{\circ}C$ ,  $800^{\circ}C$ ,  $700^{\circ}C$ ,  $600^{\circ}C$  and  $500^{\circ}C$ , and then isothermally annealed and quenched to room temperature.

Optical microscopy, scanning electron microscopy, wavelength dispersive x-ray analysis and x-ray diffraction studies were conducted to correlate structure, morphology and alloy chemistry. Based on these results it was shown that quenching after 900°C, 800°C and 700°C, isothermal annealing produced an  $\alpha + \beta$  structure. For both 600°C and 500°C, the structures obtained were ( $\alpha + \alpha$ ") and ( $\alpha + \alpha$ ") respectively. The  $\beta$ -phase in all of these cases was, of course, retained  $\beta$  and the  $\alpha$  phase could be either equilibrium  $\alpha$  or martensitic  $\alpha$ '. Based on the x-ray diffraction of the as-quenched alloys a tentative partial phase diagram for Ti-6211 was suggested.

Peak splitting was observed only on the x-ray pattern of the samples in which  $\alpha$ " was identified.  $\alpha_2$ , Ti<sub>3</sub>Al phase was not detected in this alloy in the present study.

The solute partitioning study showed that the Al-rich regions were Ta-poor and vice versa.

# Dedicated to my mother, Ezelagbo Anuka

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### CHAPTER 1

#### INTRODUCTION

Ti-6Al-2Nb-1Ta-1Mo (Ti 6211) has been developed for possible marine applications requiring thick sections. The microstructure of a near alpha or  $\alpha + \beta$  alloys such as the Ti 6211 has a great influence on various mechanical properties such as strength, ductility and fracture toughness.  $\alpha + \beta$  alloys generally (1) have good low cycle fatigue properties because of fine-grained mixture of  $\alpha + \beta$  structures with relatively high proportion of primary alpha. Fracture toughness can be improved by raising the solution temperature to give a microstructure with coarser widmanstatten alpha transformed from beta. Ductility may be achieved if beta can be retained at the same time having dispersed fine martensitic phases.

The beta-Ti alloys have been widely used for their good high strength/high toughness potential, but their major setback is that they exhibit low aged tensile ductility especially in the transverse direction of rolling (1). Hence beta-Ti alloys have restricted use especially in forgings or sheet rolling. Detailed study of alternative alloys like near  $\beta$ - or  $\alpha$  +  $\beta$  alloys is warranted.

A host of microstructural features can be produced in Ti 6211 by varying hotworking conditions, heat treatment and variations in quenching or cooling rates. Apart from the microstructural variations produced by a deliberate and controlled processing and heat treatment parameters, some uncontrolled and generally unavoidable microstructural variations result during welding, especially in thick sections. Although some of the microstructural components in this class of alloys are produced by a diffusional decomposition, there are several diffusionless and martensitic phases. Furthermore, a martensitic phase or phases can occur in these alloys, under an applied stress. Such a stress-induced martensitic transformation can occur if a metastable beta-phase exists in the alloy either due to a rapid cooling rate or a supersaturation of the beta-phase with beta-stabilizing elements at the solution treatment temperature. Depending on the heat treatment in the  $\alpha + \beta$  field, metastable beta-phase can be retained (2) in Ti 6211 alloy. A possibility exists that such a metastable beta-phase will transform martensitically. under a service load. James and Moon (3) have discussed the effects of stress-induced martensite on the mechanical properties of three Ti alloys. These authors (3) have attributed the observed low yield strengths, low values of elastic modulus and high internal friction to the stress induced martensitic transformation of the metastable beta-phase.

Recently (2) two martensites, alpha prime (hexagonal) and alpha double prime (orthorhombic) were reported for Ti 6211 alloy. However, no detailed study of the extent, formation and stability of these phases and solute partitioning at various times and temperatures has been done.

A unified investigation of the aforementioned aspects of the as-quenched and aged Ti 6211 is accomplished by the present study. In

addition accurate lattice parameters of these phases are calculated and the strain energy minimization criterion formulated by Mura et al (4) and the lattice correspondence and crystallography proposed by Mukherjee and Kato (5) are described for possible application to Ti 6211.

Although the stabilizing tendencies of aluminum, niobium, tantalum and molybdenum are known, the partitioning tendencies of these solute elements in the as-quenched structure of Ti 6211\* and other titanium alloys are not known. Solute partitioning characterization of Ti 6211 at various times and temperatures would help evaluate the effectiveness of the component elements in Ti 6211. This work also clarifies the solute partitioning tendencies in the various titanium as-quenched microstructures at various times and temperatures.

This dissertation is presented in six chapters.

Chapter 1 describes the rationale for the present study.

Chapter 2 reviews the existing literature relevant to the present study.

Chapter 3 describes the experimental procedure and techniques employed in the present study.

In Chapter 4 the results of the experiments performed are presented.

In Chapter 5 the results presented in Chapter 4 are discussed in detail with existing theories.

Chapter 6 summarizes the findings of the present study and concludes with recommendation for further research.

<sup>\*</sup>Chemical Composition (w/o): Al=5.8, Nb=2.06, Ta=0.96, Mo=0.06, Fe=0.04, C=0.03, Ti (balance).

## CHAPTER 2

### **REVIEW OF PREVIOUS STUDIES**

There is a wealth of information concerning phase transformations in titanium alloys available in the literature in recent years. Some of the information are complementary, some contradictory and others are not on a specific titanium alloy. In this review an attempt is made to bring these pieces of information under the same umbrella.

### 2.1 Titanium Alloys--An Introduction

Titanium alloys are classified into the following structural types, depending on the alloying elements, alpha or near alpha, alpha-beta; beta or near beta titanium alloys (6).

(i) The Alpha System:

Figure 1 represents a typical binary constitution diagram of alloying elements that stabilize the alpha phase. Alpha stabilizing elements are Al, Ge, Ga, C, O and N. The first three elements are of the substitutional type and the others are of the interstitial type. In the alpha-beta coexistence region, these elements are more soluble in alpha than in beta. Adding such elements to titanium stabilizes the alpha phase to higher temperatures.

(ii) The Beta System:

Alloys containing beta-stabilizers are of two types. Those which are completely miscible with the beta phase such as V, Mo, Ta, Nb are



Fig. 1. Partial Phase Diagram of the Alpha-Stabilized System.

The alpha-stabilizing elements are Al, Ge, Ga, C, O, and N.

beta isomorphous, Figure 2. Those beta stabilizers that are not miscible with the beta phase transform the beta phase in an eutectoid reaction into beta eutectoid, Figure 3. The beta eutectoid elements which decompose the beta phase into alpha and an intermetallic phase are Mn, Fe, Cr, Co, Ni, Cu, and Si.

Unlike the beta and alpha stabilizers there are neutral alloying elements, namely Zr and Sn which are extensively soluble in both alpha and beta phases. They act as strengthening agents.

Alloy Ti 6211 is composed of 5.8 w/o aluminum, 2.06 w/o niobium, 0.96 w/o tantalum and 0.6 w/o molybdenum. From the alloy element classification aluminum is an alpha stabilizer; niobium, tantalum and molybdenum are beta stabilizers.

Constitutional diagrams of Ti-Al, Ti-Ta, Ti-Nb and Ti-Mo systems are shown in Figures 4-7 (6, 95, 96).

#### 2.2 Phases and Phase Transformation in Titanium Alloys

Phase transformations and resulting phases in titanium alloys can be classified into eight groups after Murakami (8) namely,

- Decomposition of beta-phase during quenching producing alpha prime, alpha double prime, athermal omega, retained beta.
- 2. Isothermal transformation of metastable beta phase producing isothermal omega, alpha double prime, beta prime, alpha,  $\alpha_2$ ,  $\beta_2$ .
- 3. Decomposition of retained beta phase producing isothermal omega, beta prime, widmanstaten alpha, raft alpha,  $\alpha_2$ ,  $\beta_2$ , stress-induced martensite, isothermal (thermoelastic) martensite.
- 4. Decomposition of martensite producing alpha, compound, beta.





Alloying elements of the beta isomorphous type are V, Mo, Ta, and Cb.



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## Fig. 3. Partial Phase Diagram of the Beta Eutectoid System.

Alloying elements of the beta sutectoid type are Mn, Fe, Cr, Co, Ni, Cu, and Si.



Figure 4. Constitutional diagram of titanium-aluminum system.



Figure 5. Constitutional diagram of titaniumniobium (columbium) system.



Figure 6. Constitutional diagram of titaniumtantalum system.

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Figure 7. Ti-Ta Phase Diagram

- 5. Alpha-phase formation through omega and beta prime, omega  $\rightarrow$  alpha; beta  $\rightarrow$  alpha (Type 1 alpha and 2 alpha).
- 6. Eutectoid decomposition, pearlitic constituent or massive product.
- 7. Precipitation from alpha-solid solution producing compound,  $\alpha_2$ .

8. Formation of interface phase, the alpha/beta interface phase. A brief explanation of each phase shown above is given below:

- 1. Beta phase: The high temperature allotrope of titanium with a body centered cubic crystal structure (BCC).
- 2. Alpha: The low temperature allotrope of titanium with a hexagonal close packed crystal structure.
- 3. Alpha prime: A hexagonal martensite. It is a supersaturated, non-equilibrium alpha phase formed by a diffusionless transformation of the beta phase.
- Alpha double prime: An orthorhombic martensite. It is

   a supersaturated, non-equilibrium orthorhombic phase formed by
   a diffusionless transformation of the beta phase in certain
   titanium alloys.
- 5. Omega phase: A hexagonal titanium phase that forms either from quenching from  $\beta$ -phase field below the omega start temperature or isothermal aging of  $\beta$ -titanium alloys.
- 6. Athermal omega: The type of omega that forms during rapid quenching from the  $\beta$ -field to temperatures below the omega start temperature. It forms as uniform dispersions of 20-40A<sup>O</sup> precipitates.

- 7. Isothermal omega: The type of omega that forms during isothermal aging of  $\beta$ -alloys or retained beta. It is generally either ellipsoidal or cuboidal in morphology.
- 8. Isothermal (thermoelastic) Martensite: The type of martensite in which there is a balance between the strain energy generated in the parent phase and the chemical free energy made available by the lower free-energy state of the martensite phase.
- 9. Beta prime: Decomposition product of metastable beta. It is a solute lean bcc zone.
- 10.  $\alpha_2$ : Ordered phase based on Ti<sub>3</sub>Al in Ti-Al alloys with more than 10 atom a/o aluminum.
- 11.  $\beta_2$ : Ordered bcc phase formed by the decomposition of retained beta. Its formula is Ti<sub>2</sub>MoA1 in Ti-Mo-A1 alloys.
- 12. Interface phase: A beta decomposition product that forms along the alpha/beta interfaces of Widmanstatten structures.

Phase transformations and morphology in titanium alloys are summarized on Table 1-5 after Murakami (8).

#### 2.3 Morphology of Equilibrium Phases in Titanium Alloys

The nucleation and growth of alpha phase after cooling from the beta region result in a plate-like morphology of alpha which is often described as Widmanstatten structure. In alloys which have a relatively low concentration of alpha phase, these plates often form in colonies or stacks.

The formation of the colony and basketweave microstructures depends on the cooling rate from the beta or  $\alpha + \beta$  regions and the alloy chemistry. In the basketweave alpha plates with or without interleaved beta, platelets occur

# TABLE I PHASE TRANSFORMATION IN TITANIUM ALLOYS

.

	TRANSFORMATION	PROCESS
1	DECOMPOSITION OF B - PHASE DURING QUENCH-	(i) Ti Martensite : β → α', α"
	ING	(ii) Athermal $\omega$ - Phase : $\beta \longrightarrow \omega_{ath}^{+} \beta$
	DECOMPOSITION OF B -	$\beta  (\beta + \alpha) \longrightarrow \alpha^{*},  \alpha^{*}_{rich},  \alpha^{*}_{lean}$
11	PHASE IN ISOTHERMAL TRANSFORMATION	<sup>B</sup> ', <sup>B</sup> laan Type 1 G , <b>Type 2</b> G
		(i) Isothermal $\omega$ -Phase : $\beta_r \longrightarrow \omega_i + \beta_i$
	DECOMPOSITION OF	(ii) Phase Separation : Br ── B* + B
111	RETAINED S -	(iii) $\alpha$ - Phase Formation : $\beta_r \longrightarrow \alpha + \beta$ (Widmanstatten $\alpha$ , Raft $\alpha$ )
		(iv) Compound Precipitation : $B_r \longrightarrow Odered \alpha_2 + \beta$ $B_r \longrightarrow Odered \beta_2 + \beta$
	-	(v) Stress - Induced Martensite
	-	(vi) Isothermal ( Thermoelastic ) Martensite
	1	
17	DECOMPOSITION	(i) Hexagonal α' ( β - isomorphous )α + β Hexagonal α' ( β - eutectoid )
	MARTENSITE	<pre>(ii) Orthorhombic a" ( M<sub>2</sub><sup>a</sup>, &gt;&gt;room temp )→ a + β Orthorhombic a" ( M<sub>2</sub> = room temp ) : a"→ β</pre>
v	a PHASE FORMATION THROUGH INTERMEDI-	(i) β + ω → α + β
	ATE PHASE	(ii) 8 + 8' a + 8
٧I		(i) Active Eutectoid: Pearlitic Constituent ( Cellular Reaction )
		(ii) Sluggish Eutectoid: Massive Product ( Cellular Reaction )
νt	PRECIPITATION FROM	(i) Compound Precipitation
		(ii) a <sub>2</sub> Phase Precipitation
V 11	I FORNATION OF INTERFACE PHASE	α / β Interface Phase Formation during Slow Cooling

SPACE GROUP, ATOM POSITION, AND LATTICE CONSTANT	$D_{3d}^2 - P_{3m1} (D_{6h}^1 - P_{6hmm}, when u=1/2)$ (0,0,0); ±(1/3, 2/3, u): u=0.520±0.003 a= 4.607±5kX, c=2.821±3kX,c/a = 0.613 (Ti-5%Cr alloy)	
ORIENTATION RELATION	(1120) <i>u //</i> (110)g, <	0001 <b>) سلارا ای</b>
MORPHOLOGY	Athermal "	Isothermal ω
	very fine particle	ellipsoidal (low misfit, long axes∥ (lll) <sub>β</sub> ) cuboidal ( high misfit, cube face∥ (l00) <sub>β</sub> )
FORMATION MECHANISM	displacement controlled reaction	Diffusional controlled nucleation followed by displacement fluctuation
RELATION BE- TWEEN & AND W -PHASE	solute lean ∞ ► Typ	be 1 → Type 2

TABLE II OMEGA PHASE

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	τγρε Ι α	TYPE 2 a
ORIENTATION RELATION	0beying Burgers relation - (110) <sub>B</sub> // (0001) <sub>a</sub> <111> <sub>B</sub> // <1120> <sub>a</sub>	Not obeying Burgers relation {1012}{1011>twin orientation to Burgers orientation a
FORMATION	Initially formed during aging	Transformed from Type 1 after longer holding
MORPHOLOGY	Monolithic plate (ternary alloy) Monolithic needle (binary alloy)	Colony of fine particles
TRANSFORMATION MECHANISM	Nucleation and growth more like	ly than mechanical twinning

TABLE III TWO TYPES OF a - PHASE

TABLE IV V / B INTERFACE PHASE

MORPHOLOGY	CRYSTAL STRUCTURE	ORIENTATION RELATION
MONOLITHIC (Single Crystal)	fcc ( a = 436 µm ) or fct ( a = 432 µm, c/a = 1.13 )	$(0001)_{n} // (111)_{Y}$ ; $(11\overline{2}0)_{n} // (\overline{1}10)_{Y}$ $(0002)_{u} // (111)_{inc} // (110)_{B};$ $(11\overline{2}0)_{u} // (110)_{inc} // (111)_{B}$
STRIATED LAYER (Polycrystalline)	hexagonal hexagonal ( Burgers related, often twinned on {1011}n	(1010)a#(1010)p; (0001)a#(1213)p

.

# TABLE V FORMATION AND DECOMPOSITION OF ORTHOROHMBIC Q" MARTENSITE

TRANSFORMATION	PROCESS
FORMATION	i) Decomposition of Metastable $\beta$ during Quenching $\beta \longrightarrow \alpha^{"} + (\beta)$ ii) Decomposition of Retained $\beta$ by Intermediate (Bainitic)) Transformation during Isothermal Aging $\beta \longrightarrow \frac{\beta_{lean}}{\beta} + \frac{\beta_{rich}}{\beta} \propto \alpha^{"} + \beta_{rich}$ iii) Stress-Induced Transformation from Retained $\beta$ $\beta \longrightarrow \alpha^{"} + Twinned \beta$
DECOMPOSITION	i) Decomposition of $\alpha^{"}$ by both Spinodal Decomposition and Reverse Martensitic Transformation during Cooling and Aging. $\alpha^{"} \longrightarrow \alpha^{"}_{lean} + \alpha^{"}_{rich} \longrightarrow \alpha^{"}_{lean} + \beta \longrightarrow \alpha + \beta$ ii) Decomposition of $\alpha^{"}$ in the Normal Way $\alpha^{"} \longrightarrow \beta$

in colonies in a Widmanstatten structure. In colonies there are the alpha platelets having nearly identical orientations.

In addition to the above-mentioned microstructures, alpha mucleates on the prior beta grain boundary forming the grain boundary alpha ( $Gb_{\alpha}$ ). Such alpha grows rapidly along the boundary and frequently leads to a continuous layer of grain boundary alpha.

In addition to the alpha morphologies which result from nucleation and growth or from tempering of martensite, hotworking or thermomechanical processing at temperatures in the two phase alpha + beta region has an important effect on alpha-phase morphology. Thermomechanical processing results in in-situ deformation of the alpha phase which is present at the working temperature and this deformed alpha subsequently recrystallizes. The recrystallization reaction leads to the formation of equiaxed alpha particles.

#### 2.4 Titanium Alloy Martensites

Generally in quenched alloys the martensitic structure typically exhibits a plate-like morphology and in some alpha alloys a lath or packet martensite can be formed. In the plate-like martensite the individual plates each tend to have a different crystallographic orientation. This is in contrast to the colony microstructure formed by nucleation and growth in which all plates in a colony have the same crystallographic orientation.

The martensitic structure also decomposes during subsequent aging to form a relatively inhomogeneous distribution of beta-phase precipitates in a matrix of alpha.

#### 2.4.1 Hexagonal (Alpha Prime) Martensite

The most prevalent athermal Ti martensite is the hexagonal alpha prime martensite. Two morphologies of hexagonal martensite have been observed, namely massive martensite or packet or lath martensites (9,10) and acicular (10,11,12) martensite.

The massive martensite was found to consist of colonies which were resolvable optically (10). The interiors of these colonies exhibited surface relief effects; thin foil electron microscopy showed that these surface reliefs resulted from parallel martensite plates contained within the colonies, all of which belonged to the same variant of the orientation relation (10). The boundaries bewteen the plates have been shown to consist of walls of dislocations, whereas the interior of the plates contained a relatively dense tangle of dislocations (13).

The common difficulty of indirect methods employed by various workers was that an orientation relation between the martensitic product and the parent beta-phase must be assumed. Assuming the Burger relation (14) (110) beta // (0001) alpha, <111> beta // <1120>alpha the following habit planes have been obtained: iodide Ti,  $\{8,9,12\}$  beta (9), Ti-Cu,  $\{10\overline{1}1\}$ alpha (13), Zr Nb  $\{334\}$  beta (14). These results indicate that for the massive martensites habit plane may vary with alloying elements.

With increasing solute (decreasing Ms temperature) the massive martensite colony size was found to decrease (13) and at a solute concentration which was shown to vary between alloy systems the colonies totally degenerated to individual plates (12), each being a different variant of the orientation relation. This alpha prime martensite was shown to be frequently internnally twinned on (1011)  $\alpha'$ .

In sufficiently concentrated alloys an incompletely transformed structure could be produced permitting verification of the orientation relation as the characteristic Burgers relation, ie. (110)beta // (001) alpha prime, [111]beta // [1120]alpha prime (16,17,18). Habit plane determination on the acicular martensite have been performed and these martensites have, for the most part, the {334}beta habit plane (12,18,19) which had been predicted by the Bowles and Mackenzie crystallographic theory of martensite. Several workers have also reported a {344}beta (12,18) habit plane and the possible origin of this had been discussed by Hammond and Kelly (20).

The kinetics of alpha prime decomposition is rapid compared with those of the super saturated alpha phase. The dislocations in the alpha prime martensites act as heterogeneous nucleation sites.

In many systems the equilibrium precipitate in the alpha prime decomposition such as the beta-phase is heterogeneously nucleated, hence curtailing or precluding the occurrence of uniformly nucleated metastable transition precipitates. However in several beta-eutectoid systems solute-rich coherent zones have been observed during alpha prime decomposition. Such zones have been reported in Ti-Si alloys containing more than 2wt%Si (21) and Ti-Cu alloys containing about 1.5w/oCu (22). In Ti-Cu, disc zones nucleated between dislocations in the martensite substructure during aging at low temperatures. At high temperatures heterongenous nucleation of the equilibrium phase at dislocations and interfaces dominated the decomposition process.

#### 2.4.2 Orthorhombic (Alpha Double Prime) Martensite

This martensite occurs in binary alloys like Ti-Mo, Ti-Nb, Ti-W, Ti-Re and not in others like Ti-V. In alloys such as Ti-V which do not

form alpha double prime, addition of aluminum was shown to stabilize the orthorhombic phase over relatively wide composition ranges (23). Alpha double prime was recently observed in the commercial  $\alpha + \beta$ alloy Ti-6A1-2W -4Zr-6Mo and its occurrence in this alloy was shown to be accompanied by a reduction in tensile ductility (24). The lattice parameters of orthorhombic martensite were strongly composition dependent (13,23).

The decomposition of alpha double prime has been discussed by several workers (25-27) but they disagreed on the early stages of alpha double prime decomposition. Thin alpha prime platelets formed parallel to (100), (010) and (110) alpha double prime planes during the early stages of tempering of alpha double prime in Ti-W alloys (25). Bywater and Christian (26) examined the tempering of alpha double prime in Ti-Ta alloys whereas Young et al (27) examined the tempering process in Ti-6AL-2Sn-4Zr-6Mo. Both investigators suggested that the initial precipitates are beta-phase. Williams and Hickman (25) in addition presented X-ray diffraction data to support their observation and their data showed that the alpha-phase precipitation led to a simultaneous increase in the orthorhombic distortion of the alpha double prime matrix. Reexamination of the results of Young and the others shows that the time-temperature combination they have used led to a fairly advanced stage of decomposition. The Ti-W system studied by Williams and Hickman is a eutectoid system while the Ti-Ta and Ti-6Al-2Wn-4Zr-6Mo are isomorphous systems. Thus the composition changes required to precipitate beta-phase in the latter

system should be much smaller than the Ti-W system where the beta-phase is essentially pure tungsten. In view of this, it was suggested that the  $\alpha$ " +  $\alpha$ " +  $\alpha$  decomposition might be peculiar to the Ti-W system (28).

The end result of alpha double prime decomposition during tempering is generally agreed to be  $\alpha + \beta$ . Two distinct modes of formation of this mixture are the cellular reaction and the heterogenous nucleation of beta-phase similar to that seen in the case of alpha double prime.

Davies et al (29) recently proposed that the transition in martensite crystallography from hexagonal alpha prime to orthorhombic alpha double prime occurred with increasing solute content and hence decreasing Ms, and that at least one alpha double prime point of inflection must exist in the alpha double prime free energy. They proposed a form of the free energy/composition relationships for alpha prime, alpha double prime and beta phases at a certain temperature within the  $\alpha + \beta$  field, and also the corresponding phase diagram showing the chemical spinodal of alpha double prime and Ms of the beta phase.
## 2.4.3 Crystallography of $\alpha'$ and $\alpha''$ Martensites

The Burger's mechanism for the beta (BCC)  $\rightarrow$  alpha prime (hcp) (14) Fig. 8 transformation in Titanium alloys is still tenable. Also the formation of the alpha double prime (the orthorhombic phase) and alpha prime can be explained in terms of the beta-stabilizing element composition and simple atomic shuffling.

Oka and Taniguichi (30) found that with increasing Mo content a beta-stabilizer, the lattice parameter of the stress induced orthorhombic phase approached that of the beta-phase. Sasano et al (31) confirmed that with increasing beta-stabilizing agent the crystal structure of titanium martensites changes from hcp to orthorhombic. T. W. Duerig et al (32) and Sasano et al. tried to explain beta  $\rightarrow$  alpha prime or alpha double prime by simple atomic movements. Duerig et al (32) reported the following atom positions of the orthorhombic alpha double prime martensite in a Ti-10V-2Fe-3AL alloy: (0,0,0); (a/2, b/2, 0), (0,2b/3, c/2); (a/2, b/6, c/2). The lattice parameters of the orthorhombic cell is reported to be: a =  $3.01A^{0}$ 

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b = 4.83A^{0}
c = 4.62A^{0}
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In addition to alpha prime and alpha double prime, f.c.o. (face centered orthorhombic) martensite was obtained in Ti-12V alloy bulk crystal (33). It has been pointed out that all the titanium martensites (alpha prime, alpha double prime, f.c.o.) can be generated from a face centered tetragonal equivalent of the four unit cells of the b.c.c. beta phase (Figure 9).





Mukherjee and Kato (5) unified these physical interpretations of beta  $\rightarrow$  alpha prime or alpha double prime and proposed that for the alpha prime, the Bain strain is brought about by Burger's mechanism where the operation of the  $\{112\}$   $<111>_{\beta}$  shear systems followed by a small volume increase results in the (0001)<sub> $\alpha'</sub>$  plane from the (011)<sub> $\beta$ </sub> plane. In addition to the above Bain strain a a<sub> $\beta$ </sub> [01T]/6 shuffling on every other (011)<sub> $\beta$ </sub> plane is necessary to create the h.c.p. structure.</sub>

The formation of alpha double prime martensite can be explained in the same way. The difference lies in the fact that after the operation of the {112} <111><sub> $\beta$ </sub> shears, the (011)<sub> $\beta$ </sub> plane does not completely change into the hexagonal close packed plane but stops midway between the (011)<sub> $\beta$ </sub> and (0001)<sub> $\alpha$ </sub>, leaving the angles  $\theta_1$  and  $\theta_2$  Figure 10 slightly different from 120 degrees. Thus the alpha double prime martensite can be considered a "distorted" alpha prime martensite. In the case of f.c.o. martensite no shuffling is necessary and the lattice correspondence was very similar to that in Au-Cd martensite (33). From the Bain strains calculated in Ti-12.6V by Mukherjee and Kato (5) for the f.c.o. martensite it is conclusive that f.c.o. martensite unlike alpha prime and alpha double prime cannot be considered a "distorted" alpha prime martensite.

Sasano et al (31) and other investigators have demonstrated that orthorhombic phase x-ray line derives from the hcp line with increasing Mo or beta-stabilizing element, for example in Ti-Mo-3 w/o Al, for 0 to 5 w/o Mo the hcp 10T0 line is intact, but for 6 w/o to 12 w/o Mo the hcp 10T0 line split into {110} and {020} orthorhombic lines, the {10T1} hcp lines split into {111} and {021} orthorhombic lines and the separation



Figure 9. Lattice correspondence of martensites showing the four unit cells of the b.c.c. crystal and its face-centered tetragonal equivalent.



Figure 10. Crystal structure change from B.C.C. to alpha prime and alpha double prime, after Mukherjee and Kato (5).

between these twin orthorhombic lines increased with increasing Mo content. The {020} and {111} lines of the orthorhombic approached gradually the {002} of orthorhombic or {110} of bcc respectively as Mo content became higher. Alpha double prime was difficult to retain in thin foil form, however it was found to be internally twinned in a Ti-8.5 Mo-0.5Si on {111} planes (25).

#### 2.4.4 Other Titanium Martensites

#### 2.4.4.1 Face centered tetragonal martensite

In addition to the well known alpha prime and alpha double prime titanium martensites, several workers have observed face-centered tetragonal martensite with c/a ratio nearly unity in Ti-Fe (35), Ti-Cr (16), complex ternary titanium alloy (35) and quartenary titanium alloys (34,24). This martensite was reported on the basis of thin foil electron microscopy evidence; recent evidence obtained by Williams and Rhodes shows that this martensite is orthorhombic in its bulk form (24). For example, if a Ti-14V-6A1 alloy was guenched from  $900^{\circ}$ C, X-ray diffraction evidence obtained from bulk samples showed that this allow contained orthorhombic martensite, whereas electron microscopy examination of thin foils prepared from the same sample used for X-ray diffraction showed evidence of face-centered cubic martensite. Furthermore, light microscopy of the thin edge of the electron microscopy specimens showed a marked rumpling characteristic of shears resultant from mechanical instability along the thin edges of the foils (24). In other alloys which have bulk orthorhombic martensite, thin foil results showed that the martensite reverted to the bcc, beta-phase along the edge of the foil during thinning. Thus the balance of the evidence at present indicates that the face-centered cubic and/or face-centered tetragonal martensites

reported by several workers on the basis of thin foil electron microscopy evidence, are in fact thin foil version of a bulk orthorhombic martensite. Oka et al (33) referred to earlier again reported a face-centered orthorhombic martensite on Ti-11.6wt%V. alloy.

### 2.4.4.2 Stress-induced products

There is conflicting evidence regarding the nature of martensite produced in metastable bcc Ti alloy during stressing.

In some alloys, clear evidence for mechanical twinning (36,37) has been presented while evidence for a stress induced martensite has been obtained in other alloys (24,37). It appears that the concentration and type of solute has an important influence on whether the stress-induced product in a given alloys is twinning or martensite. Electron microscopy of Ti-11.5Mo-4.5Sn-6Zr (B-III); Ti-14Mo-3A1 (24,36) showed the occurrence of bcc twins in these alloys. Also for some other alloys the fact that {122} <111> twinning (37,38) and {322} twinning (36,39) could occur during stressing of metastable bcc alloys was verified. There is good evidence to show that other alloys do form stress-induced martensite and in these cases the martensite product has been shown to have orthorhombic structure. Koul and Breedis (40) reported a contrary evidence of a hexagonal stress induced product in Ti-V and Ti-Mo alloys. However if one considers the relatively orthorhombic distortion which can occur in some alloys like Ti-10at%Al+V (41) this difference can be resolved thus; the separation between the (110) alpha double prime and (020) alpha double prime and the (111) alpha double prime and (021) alpha double prime is sufficiently small that high resolution X-ray diffraction is required to differentiate between a hexagonal and an orthorhombic product.

Additionally, in the present case; the straining results in some line broadening which makes resolution difficult. Williams (41) studied the above subject involving 25-50 different alloy compositions including those in which hexagonal stress induced martensites have been reported and was unable to reproduce the hexagonal stress-induced martensite but observed the orthorhombic alpha double prime phase.

The factors which control the occurrence of twinning or martensite formation during stressing are not clear but it appears that Al addition to Ti-Mo and Ti-V alloys promotes stress-induced alpha double prime. Blackburn and Feeney (36) analyzed the occurrence of the {112}<sub> $\beta$ </sub> and {332}<sub> $\beta$ </sub> twin modes and found that alloys in which the parent bcc betaphase contained athermal omega-phase exhibited {332} twinning, whereas more concentrated alloys characteristically twinned on {112}<sub> $\beta$ </sub> (38).

In a number of beta-alloys,  $M_d$  lies above room temperature. As a result, stress-induced reactions have been reported in the betastabilized Ti-Mo (42) and Ti-V (40) systems as well as in other complex systems. The structure of the stress-induced martensitic products in beta-Ti alloys was reported as FCC (35), HCP (43), and recently as orthorhombic (44,45). T. W. Duerig et al (32) studied the stressinduced transformation in Ti-10V-2Fe-3A1. They conclusively found that the transformed microstructure contained orthorhombic martensite (alpha double prime) and the martensite plates were accompanied by mechanical twinning. The orientation relationship between this martensite and beta-matrix was shown to be

 $(110)_{\beta} // (001)_{\alpha''}$  $[1\bar{1}]_{\beta} // [110]_{\alpha''}$ 

Darkfield imaging (32) of alpha double prime spots showed the martensitic plates to be "mottled" or "spotty."

Oka and Taniguchi (30) in their study of the crystallography of stress-induced products of some Titanium alloys again found SIM (stress-induced orthorhombic martensite) and a {332} twin of the beta-matrix in Ti-9 ~16%Mo deformed by compression or cold rolling. SIM formed in Ti-9 ~11%Mo had their habit planes close to {443} plane.

### 2.5 Omega Phase

In alloys where the martensite reaction is suppressed by sufficient concentration of beta-stablishing elements which depress the martensite finish temperature beneath room temperature, beta-phase can be retained in metastable form by quenching.

In such alloys the beta-phase was shown by Silock et al (46) and Bagarjatskii et al (47) to partially decompose during quenching into a metastable precipitate called omega-phase.

Athermal omega was considered for sometime to form by a martensitic transformation largely because its formation could not be suppressed by quenching. Blackburn and Williams (37) using Electron microscopy showed that athermal omega occurred as extremely small (20-40A<sup>0</sup>) particles with a very high density. Such a product is not compatible with existing theories of martensitic transformation since the key features such as habit plane cannot be assigned to such small particles. It thus appears that athermal omega is not a martensitic product at least in the classical sense. A new class of transformation called displacement controlled transformation, was proposed by de Fontaine (48) who used omega as an example of such a transformation.

Paton, de Fontaine and Williams (56) used cold storage transmission electron microscopy to show that the omega-phase could be reversibly formed on cooling beneath room temperature. Such reversibility is consistent with a displacement controlled transformation which occurs without change in composition. The displacement controlled reaction argument can also account for a related phenomenon, namely the complex distribution of diffuse scattering which is observed in beta-alloys. The streaking has been ascribed to random or uncorrelated displacements of the atoms so that the omega-phase lattice is not generated but the periodicity of the bcc lattice is reduced.

The athermal omega-phase was shown to be trigonal in heavily betastabilized alloys but became hexagonal in leaner alloys (49).

The formation mechanisms of athermal omega has been suggested to be displacement-controlled reaction while that of isothermal omega was diffusion controlled nucleation followed by displacement fluctuation (50-54). Recently Duerig et al (55) suggested that a composition alloy invariant growth mechanism does not differ from "classical" diffusion controlled growth, that as the alloy content becomes leaner or the betastructure less stable, the compositionally invariant growth mechanisms begin to dominate and a certain "unusual" growth phenomenon can be observed, which distinguishes the beta → omega reaction from most others. They observed a morphology transition from ellipsoids to cuboids in Ti-10V-2Fe-3Al at a constant size. Hence they proposed that the morphology change could result from a rapid, chemically invariant omega particle growth, followed by a slow composition equilibration. There is evidence that athermal omega-phase reverts during reheating to the isothermal aging temperature to much lower density isothermally formed particles.

This suggests that each athermal omega-particle does not act as a pre-existing nucleus for isothermal omega-phase. Also the incubation period which preceded the isothermal omega-phase formation as shown in (54) suggests that the athermal omega-phase was reverted and the isothermal omega-phase formed by nucleation and growth.

The similarity between bcc beta-phase and the hexagonal omega-phase (48,56) can account for the athermal  $\beta \neq \omega$  transformation. It would also result in a low barrier to nucleation and subsequent growth which would lead to rapid precipation kinetics of isothermal omega-phase. Both athermal and isothermal forms of omega-phase are coherent, this also reflects the similarity between beta and omega.

Isothermal omega phase is produced by isothermal aging of alloys that are relatively dilute as well as alloys richer in beta-stabilizing alloy additions. Isothermal omega-phase was shown to have a cuboidal or ellipsoidal morphology depending on the precipate/matrix misfit (57,58). It was observed that the isothermal ellipsoidal omega has low precipate/ matrix misfit, its long axis are parallel to  $<111>_{\beta}$  and cuboidal omega has high misfit the cube face is parallel to  $(100)_{\beta}$ . This misfit arises in the isothermal case because the omega-phase is solute lean and therefore leads to enrichment of the beta-matrix.

The effect of ternary additions of Zr, Sn, Al and oxygen on the occurrence and stability of isothermal omega-phase was studied (59). The elements reduced the occurrence and/or stability of omega-phase. Both Sn and Zr increased the stability of beta-phase when present together with other beta-stabilizers like Mo or V and thus these elements reduced volume fraction of omega-phase. Al promoted early separate

nucleation of the alpha-phase and the occurrence of this competitive reaction product also reduced the time of stability of omega-phase by consuming it via diffusional growth of the alpha-phase.

## 2.6 Interface Phase

A reaction product which has an apparent close relationship to the type 1 and type 2 alpha-phase formation is the interface phase. This is a reaction product which forms along the alpha/beta interfaces of Widmanstatten structures in alloys such as Ti-6Al-4V. The interface phase has a somewhat variable morphology (60). It forms in extensive quantities during continuous cooling from temperatures above 950°C. Attempts to produce and control this product by isothermal reaction studies were unsuccessful and it appeared that it only formed athermally (61,62). The reasons for this are not clear at present. In addition, the nature of the interface phase is still subject to discussion. Rhodes and Williams (60) suggested that it is a heavily twinned and dislocated region of the Widmanstatten alpha plates. The interpretations are tied to each of these investigators' suggested mechanism of interface phase formation and each has some difficulties associated with it. For example, Rhodes and Williams (60) suggested that the interface phase is a nucleation and growth product, but if this is the case, the apparent athermal character of the reaction is difficult to explain. Margolin et al (63) suggested that the interface phase forms as a result of mechanical twinning which arise because of stresses at the interface which are created by thermal expansion mismatch of the alpha and beta phases. If this is true, then one might expect the interface phase to be very sensitive to cooling rate. This does not appear to be

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the case as shown in (61). Secondly, if the interface phase is simply localized mechanical twinning, then each twin should have accomodation dislocations in the matrix ahead of its terminus; this generally is not the case. Finally, Rhodes and Williams (60) reported a monolithic facecentered cubic layer of the interface phase which formed at intermediate cooling rates. It is possible that this is a transition reaction product which subsequently decomposes into the striated, hexagonal interface phase.

Recently Chenu et al (64) found that in Ti685 the alpha/beta interface phase was of two forms, the monolithic (ML) and a striated (SL) layer and was dependent on homogenisation temperature in the  $\beta_0$  or  $\alpha + \beta$  fields and the cooling rate. The layers have f.c.c. crystallographic structure and in twin relationship with the <111> ML twin axis. The formation of the interface and its width was influenced by the Mo content of the beta phase and the cooling rate. The ML and SL layers have identical composition. Two different orientation relationships were found between ML, beta and alpha phases in the same sample

- 1.  $\{110\}_{\beta} // \{0001\}_{\alpha} // \{111\}_{ML}$ <111><sub>B</sub> // <1210><sub>a</sub> // <110><sub>ML</sub>
- 2 (110)<sub> $\beta$ </sub> // (0001)<sub> $\alpha$ </sub> // (001)<sub>ML</sub> <111><sub> $\beta$ </sub> // <1210><sub> $\alpha$ </sub> // <110><sub>ML</sub>

Banerjee and Arunachalam (65) in their study of two Titanium alloys IMI 685 and BT9 maintained that the f.c.c. interface phase does not form as part of the transformation sequence beta + f.c.c + alpha, it rather had precipitated on the alpha side of the alpha/beta interface at a fairly late stage of the beta + alpha transformation. They concluded that beta is retained whenever the beta + alpha transformation occurs

by nucleation and growth and the interface phase is observed at all alpha lath/retained beta interfaces, but not when the beta + alpha transformation is martensitic, the f.c.c. interface with lattice parameter of 404A<sup>0</sup> exists in two crystallographic orientation relationship to alpha, namely  $(1\overline{10}) // (1\overline{100})_{\alpha}$ ;  $[001] // [0001]_{\alpha}$  and  $(111) // (0001)_{\alpha}$ ;  $[1T0] // [11\overline{20}]_{\alpha}$ , type I and type II f.c.c. respectively. They suggested that the f.c.c. phase is a hydride of titanium because there is no f.c.c. based phase in any binary systems of their alloy concentration levels except for gamma-hydride, the lattice parameter of the f.c.c. phase is in close agreement with that of gamma-hydride, and alpha are identical to those observed between hydride and alpha.

### 2.7 Decomposition of Supersaturated Phases

There are two principal modes of decomposition of the supersaturated alpha phase: precipitation of a second phase and ordering of alloys whose composition is in the 25at%Al range. The principal products of the precipitation reations are the ordered  $\alpha_2$  phase, intermetallic compounds, such as Ti<sub>2</sub>Cu or Ti<sub>5</sub>Si<sub>3</sub>; the hydride phase, TiH<sub>2</sub>; and compounds which are based on the rare earth elements such as Y or Er.

# 2.7.1 a, Formation

The alpha-phase which contains more than 10at.%Al is supersaturated and can decompose during aging at 500<sup>0</sup>C.

This decomposition of supersaturated Ti-Al alloys containing 10at%Al has been observed by many workers (66,67) and there is general agreement that the decomposition product is an ordered phase based on Ti<sub>3</sub>Al. This product is usually designated the  $\alpha_2$  phase and has a DO<sub>19</sub> structure.

Only relatively recently it was shown that the  $\alpha_2$  phase formed as uniformly distributed, coherent precipitates (67). Further, the exact position and extent of the  $\alpha + \alpha_2$  phase field is still subject to some question. The morphology of coherent  $\alpha_2$  during early stages of formation is equiaxed whereas at later stages (larger sizes) it is ellipsodial with the long axis lying along the 'c' axis of the matrix and precipitate. This morphology can be accounted for by considering the precipitate misfit, which is 0.35% parallel to [0001] and 0.83% perpendicular to [0001]. It has been shown that the precipitate aspect ratio and particle size limit for coherency can be altered by the addition of ternary solutes such as Sn and Ga (68). Of these, Sn causes the  $\alpha_2$  misfit to become more isotopic whereas Ga causes it to become more directional and larger along the 'a' axis. As a result, the  $\alpha_2$  phase is nearly equiaxed in Ti-Al-Sn alloys and forms a long, slender, semi-coherent rods in Ti-Al-Ga alloys.

Another variable which influences the formation of  $\alpha_2$  in Ti-Al alloys is the amount of oxygen present as an impurity. Paris and Williams recently investigated the role of oxygen in  $\alpha_2$  formation (69) and found that a 2000 wt ppm increase in oxygen content in a Ti-7.3wt%Al alloy led to an increase of  $100^{\circ}$ C in the coherent  $\alpha/\alpha + \alpha_2$  solvus position. The reasons for this are not clear at present but several factors pertain. First oxygen expands the alpha-Ti lattice which increases the misfit of the  $\alpha_2$ , at least when the unconstrained lattice parameters of the "pure" alpha and  $\alpha_2$  phases are considered. This would be expected to suppress the coherent solvus rather than raise it. Gehlen (70) has suggested that the structure of the  $\alpha_2$  phase is distorted and he has used x-ray diffraction measurements and intensity calculations

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to support this. Assuming that the distortion described by Gehlen really exists, some of the octahedral holes in the  $\alpha_2$  lattice will be expanded. This tends to increase solubility of oxygen in the  $\alpha_2$  phase. On this basis, Paris and Williams (69) suggested that oxygen partitions to the  $\alpha_2$  phase and stabilizes it to higher temperatures.

### 2.7.2 Beta-Phase

In alloys which contains between 7 and 25at%Al the addition of sufficient quantities of beta-stabilizing elements still permits retention of the bcc allotropic form during quenching. This Al rich beta-phase exhibits several decomposition modes which are somewhat different from those of the lower Al beta-phase. In a Ti-16at%Al-7at%Mo alloy the metastable beta-phase decomposed to form an ordered bcc precipitate (71) designated  $\beta_2$  (72). The  $\beta_2$  phase forms as a fine, uniform dispersion of ordered, coherent precipitates in a disordered bcc matrix. By contrast to the Ti-Mo-Al alloy described above, in Ti-Nb-Al and Ti-Nb-W-Al alloys containing 25at%Al the beta-phase transformed to 100vol%  $\beta_{2}$  during quenching (73-75). This beta-phase contains fairly large thermal antiphase domains; this suggests that the orderdisorder temperature for formation of the  $\beta_2$  (CsCl) structure is reasonably high so that growth of the ordered domains occurs until they impinge leaving a fully transformed structure. Although the order-disorder temperatures have not been experimentally determined in these alloys, the following explanation for the differences between Ti-Mo-Al and Ti-Nb-Al is suggested. The effect of Mo on the suppression of the beta  $\rightarrow$ alpha transus temperature is much greater than that of Nb. Thus the

beta-phase is stable to lower temperatures in the Ti-Mo-Al alloy. As a result, beta-phase instability will occur at a lower temperature where diffusion is slower in the Ti-Mo-Al alloy. This may limit the extent of ordering kinetically. In the alloy compositions in which the ordered bcc phase is observed, it becomes unclear which types of atoms occupy  $\prec$  the A and B sites in the AB supperlattice. Even if it is assumed that  $\prec$ Ti occupies the A sites and all other solutes occupy the B sites, there typically are insufficient B atoms to achieve stoichiometry. For example, the ordered bcc phase was observed in Ti-25at%Al-10at%Nb and in Al-25at%Al-%at%Nb-lat%W yet in these alloys the total Al + Nb or Al + Nb + W amounts to less than 50at%. Therefore, the B2 lattice must be stable over a wide composition range. Selected area electron diffraction patterns obtained from as-quenched samples showed extensive streaking along  $(110)_{B2}$ . Bouchard and Thomas (76) reported similar effects in  $(Cu-Mn)_3$ Al alloys where a B2 lattice decomposed into a  $L2_1$  phase and a  $D0_3$ phase. It is possible that a similar decomposition reaction is occurring in Ti-Al-Nb alloys. Further work to examine this point is warranted. The equilibrium structure of the Ti-Al-Nb system is  $\alpha_2$  (DO<sub>19</sub>) +  $\beta$ (Bl) and thus is different from that of the  $(Cu-Mn)_3$  Al alloys which is  $Cu_3AL (DO_3) + CuMnA1 (L2_1)$ . Thus if the B2 + L2<sub>1</sub> reaction does occur in the Ti base system, it must be a metastable state relative to  $\alpha_2 + \beta$ .

### 2.8 The Phenomenological Crystallographic Theory of Martensitic Transformation

The phenomenological crystallographic theory of displacive martensitic transformations was developed simultaneously by Wechsler, Read and Liberman (77) and Bowles and MacKenzie (78). In 1924 Bain (79) suggested

that the bcc structure of iron can be produced from the fcc by a contraction of about 17% in the direction of one of the austenite cube axes and an expansion of about 12% in the plane perpendicular thereto, Figure 11. This Bain Model and many other theories summarized by Cohen (80) were not able to account for all of the important crystallographic features of martensitic transformation in a self-consistent general manner, that is, if the crystal structure change was correctly described, the habit plane and/or orientation relationship usually was not.

The Wechsler, Lieberman and Read theory (W-R-L) asserts that the crystallographic features of martensite transformation can be completely explained in terms of three basic deformations:

1. A Bain distortion, which forms the product lattice from the parent lattice, but which in general does not yield an undistorted plane that can be associated with the habit plane of the deformation.

2. A shear deformation which maintains the lattice symmetry (does not change the crystal structure) and, in combination with the Bain distortion, produces an undistorted plane. In most cases, this undistorted plane possesses a different orientation in space in the parent and product lattices.

3. A rotation of the transformed lattice, so that the undistorted plane has the same orientation in space in both the parent and product crystals, Figures 11, 12, 13.

No attempt wasmade in W-L-R theory to give physical significance to the order of the steps listed above and the entire theory is best viewed as an analytical explanation of how one lattice can be formed from the other.



Figure 11. Lattice correspondence and distortion proposed by Bain (79) for the FCC+BCC (BCT) martensitic transformation in ferrous alloys. The correspondence cell (heavy lines) in the parent phase becomes a unit cell of martensite after a homogeneous lattice deformation. The principal distortions along x', y', and z' are indicated.



Figure 12. Schematic representation of inhomogeneous lattice-invariant shear by (a) internal twinning and (b) internal slip within martensite plates after (81).



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Figure 13. Sphere-ellipsoid representation of homogeneous deformation in which matching planes of no distortion exist (cross-hatched) after (81).

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On the other hand Bowles and MacKenzie (78) B-M theory, almost identical but mathematically somewhat different to the W-L-R theory, has adjustable parameters in the form of a uniform dilation in the interface (habit plane). The surface dislocation approach of Bullough and Bilby (82) is mostly closely related to the matching method of Frank (83) and Bilby and Frank (84). For excellent summaries and critical reviews of the theoretical and experimental work on martensitic phase transformation the reader is referred to Bilby and Christain (85) and Cohen (80).

## 2.8.1 <u>Mathematical Formulation of the Martensitic Transformation-</u> Large Deformation Theory (81)

The basic equation of B-M (78) and W-L-R (77) theories can also be presented in matrix form for completeness thus:

Although equation (1) shows the inhomogenous shear S following the Bain distortion, the same mathematical result is obtained by "allowing" the shear to occur in the parent phase prior to the Bain distortion. By the latter reasoning the basic equation becomes

 $E = R B S \dots (2)$ where S, like  $\overline{S}$  represents a simple shear.

In the formulation by Wechsler, Lieberman and Read (77) RB is the lattice deformation part of the observed shape change, while  $\overline{S}$  is the

fine-scale inhomogeneous part. Although the operation of  $\overline{S}$  may not be apparent from the macroscopic homogeneity of the shape deformation, there is now ample evidence from electron microscopy that such latticeinvariant deformation do occur on a fine scale.

The equation E = R B S can be rewritten as proposed by Bowles and MacKenzie (78)

 $E S^{-1} = R B = lattice deformation.$  (3)  $S^{-1}$  corresponds to a shear deformation of the same magnitude and on the same plane as S, but in the opposite direction. It can be regarded as the invisible portion of the lattice deformation which is cancelled by S, and is sometimes called the complementary shear.

With reference to the lattice correspondence in Ti 6211 in the beta martensite transformation

$$a_{\beta} + a_{\alpha},$$
$$a_{\beta}\sqrt{2} + b_{\alpha},$$
$$a_{\beta}\sqrt{2} + a_{\alpha},\sqrt{3}$$

the Bain distortions

$$n^{1} = a_{\alpha'}/a_{\beta}$$
  
 $n^{2} = b_{\alpha'}/a_{\alpha}/2$   
 $n^{3} = a_{\alpha'}/3/a_{\beta}/2$ 

Thus the Bain distortion for BCC  $\rightarrow$  HCP can be written as

	a <sub>α</sub> ,/a <sub>β</sub>	0	0 ]									
B =	0	b <sub>α</sub> ,∕a <sub>β</sub> √2	0	•	• •	•	•	•	•	•	•	(4)
	0	0	$a_{\alpha}$ , $\sqrt{3}/a_{\beta}$ 2									

This B-matrix does not have an undistorted plane and so cannot conform to the invariant-plane condition.

The IPS shape deformation (E) can be expressed as (78)

By means of B-M theory (78) the invariant line strain can be calculated if the Bain distortion is known (from the correspondence and lattice parameters) and if the inhomogeneous shear mode) that is the plane and direction) is presumed.

 $S^{-1}$  in equation (3) being a simple shear is also an IPS and the product  $ES^{-1} \equiv L \equiv RB$  is an invariant line strain, defined by the intersection of the two planes which are invariant to E and  $S^{-1}$  respectively.

The crystallographic concepts and their mathematical formulation presented have both successes and discrepancies. A departure from the basic IPS criterion has been introduced in the form of a "dilatation parameter" (78) to improve the agreement between the predicted and measured habit-plane orientations. This empirical adjustment relaxes the requirement that the habit should be undistorted, and so the shape deformation is not a true IPS. There would be no way to physically justify the existence of such arbitrarily determined parameters. Other attempts to account for such difficulties have included the assumption of two or more inhomogeneous shear systems (86,87). However, it was pointed out by Kato (88) that the introduction of three independent IPS's in the phenomenological theory makes any arbitrary plane as a habit plane. Thus, the introduction of such new adjustable parameters is both dangerous and meaningless.

## 2.8.2 Phenomenological Analysis Based on the Strain Energy Minimization Criterion--Small Deformation Theory

Mura et al (4) and Kato et al (89) have shown that there is a one-to-one correspondence between the phenomenological crystallographic theory of martensitic transformations (78) and the strain energy minimization approach based on the small deformation theory (4, 89). According to this analysis, if the transformation strain  $\varepsilon_{ij}^{T}$  (Bain strain plus lattice invariant strain) in  $X_1 - X_2 - X_3$  Cartesian coordinate system satisfies the condition.

the strain energy becomes minimum (zero) and the condition in equation 6 with the  $X_3$  - axis as an invariant plane (habit plane) normal, is equivalent to the invariant plane condition in the pehnomenological theory. The advantage of using the small deformation theory is that the calculation becomes much simpler and even if the three principal components of the Bain strain are different, such as the case in the Titanium martensites, the final solutions can be obtained in simple analytical forms. Mukherjee and Kato (5) applied this strain energy theory to analyze the crystallography of the alpha prime, alpha double prime and face-centered orthorhombic martensites. The Bain Strain in the t-system for the three martensites can be written in the form of

 $\varepsilon_{ij}^{1} = \begin{bmatrix} \varepsilon_{1} & 0 & 0 \\ 0 & \varepsilon_{2} & 0 \\ 0 & 0 & \varepsilon_{3} \end{bmatrix}_{t}^{1}$ 

the Bain distortion,  $\eta = \varepsilon + 1$ .

They found that  $\varepsilon_1 < 0$  (contraction),  $\varepsilon_2$ ,  $\varepsilon_3$ , > 0 (expansion for the orthorhombic (alpha double prime) and the hexagonal (alpha prime) martensites whereas  $\varepsilon_1 > 0$  and  $\varepsilon_2$ ,  $\varepsilon_3 < 0$  for the f.c.o. martensites. If equation 7 is viewed based on the x-y-z system in the parent beta phase (beta system) shown in Figure 9 the following equation results

$$\varepsilon_{ij}^{1} = \begin{bmatrix} \varepsilon_{1} & 0 & 0\\ 0 & (\varepsilon_{2} + \varepsilon_{3})/2 & (\varepsilon_{3} - \varepsilon_{2})/2\\ 0 & (\varepsilon_{3} - \varepsilon_{2})/2 & (\varepsilon_{2} + \varepsilon_{3})/2 \end{bmatrix} (Variant 1)$$

It has been reported that the lattice invariant shear for each martensite occurs dominantly by twinning and the twinning planes are  $\{10\overline{1}1\}$  alpha prime, (20)  $\{111\}$  alpha double prime (29) and  $\{111\}$  f.c.o. (33). All these twinning planes correspond to the (110) beta plane of the parent beta-phase Figure 9. Thus by using the beta system, the twinned variant should have the Bain Strain of

$$\varepsilon^{2}_{ij} = \begin{bmatrix} (\varepsilon_{2} + \varepsilon_{3})/_{2} & 0 & (\varepsilon_{2} - \varepsilon_{3})/_{2} \\ 0 & \varepsilon_{1} & 0 \\ (\varepsilon_{2} - \varepsilon_{3})/_{2} & 0 & (\varepsilon_{2} + \varepsilon_{3})/_{2} \end{bmatrix}$$
 (Variant 2)  
From equations 6, 7 the total transformation strain ,  $\varepsilon^{T}_{ij}$  can be written

as

If the unit vector  $\vec{h}$ , normal to the habit plane is written in the beta system as

invariant plane condition of equation 6. In this new system  $\hbar$  becomes parallel to the X<sub>3</sub>-axis. Equation 6 gives three simultaneous equations with f,  $\theta$  and  $\phi$  as the three unknown parameters. Solving these equations these results are obtained

$$f = \frac{1}{2} \pm \frac{A^2 - 4AB}{2A}$$

$$A = \{3\epsilon_1 \ (\epsilon_2 - \epsilon_3)^2 + 2(\epsilon_1 - \epsilon_2) \ (\epsilon_2 + \epsilon_3) \ (\epsilon_1 - \epsilon_3)\}\epsilon/4 \ . \ . \ (14)$$

$$B = -\epsilon_1\epsilon_2\epsilon_3$$

The authors Mukherjee and Kato (5) showed that solutions corresponding to the positive and negative signs in equation 14 are crystallographically equivalent. Also, it should be noted that there are two independent (crystallographically different) solutions for the orientation of the habit plane, depending on the positive and negative values of  $\tan \phi$  in equation 12. Using the Bain strains the authors calculated the habit plane normal. The volume fraction of the variant 1 were calculated from equations 12 through 14 for each of the three martensites.

This present analysis was compared for the case of alpha prime martensite in Ti-Mn with that of Knowles and Smith (91) who based their analysis on the phenomenological theory and essentially the same orientation of the habit plane normals are predicted, one of the solutions belonging to the class A ( $\alpha$ +,  $\omega$ +) and the other to the class A ( $\alpha$ -,  $\omega$ +) in B-M notation (92) Figure 14. From this comparison the authors (5) concluded that the small-deformation theory which does not involve any numerical calulation can be used in lieu of the phenomenological theory to discuss the crystallography of the titanium alloy martensites.

Furthermore it has been found that in Ti-Mn alloys (20,91) there are two different types of alpha prime, one with the  ${334}_{R}$  and the other with the  ${344}_{B}$  habit planes. None of these two solutions for the alpha prime accurately explains the above habit plane indices. Hammond and Kelly (20) were thus forced to use an adjustable "dilatation" parameter,  $\delta$ , in the phenomenological theory to bring the irrational habit plane normals to the observed indices. Knowles and Smith (91) analyzed the zig-zag parent-martensite interface in the {344}  $_{\rm \beta}$  martensite on the basis of the Burgers vector minimization criterion of the interface dislocations. According to their calculation the total magnitude of the Burgers vector averaged over the entire interface becomes zero, in other words no long range strain field is created due to the transformation and the invariant plane condition in the macroscopic habit plane is still satisfied in this model. Thus, the orientation of the calculated habit plane on the average remains the same as that predicted from the phenomenological analysis shown in Figure 14.

The reason adduced by Mukherjee and Kato (5) for the discrepancy between the calculated orientations of the habit plane and the observed  $\{334\}_{\beta}$  or  $\{344\}_{\beta}$  is that Hammond and Kelly (20) as well as Knowles and Smith (91) used the lattice parameter of the beta phase at room temperature. Since beta + alpha prime martensitic transformation takes place at a higher temperature the lattice parameter should be compensated by taking into account the thermal dilatation. Davies et al (29) on the other hand have systematically obtained the lattice parameters of the beta



Figure 14. Calculated habit plane normals for titanium alloy martensites, Mukherjee and Kato (5).

observation, the alpha prime martensite formed in the alloy with as much as 4% molybdenum and the alpha double prime martensite formed in Ti-6% molybdenum and Ti-8% molybdenum. Similar tendency from hexagonal to orthorhombic structure change associated with increasing betastabilizing elements was reported in other titanium alloys (31).

Mukherjee and Kato further calculated the Bain strains for Ti-Mo from the lattice parameters of the beta and the martensitic phases and applied the strain energy minimization criterion and found as shown in Figure 15 that the habit plane normals lie close to the  $[\bar{4}\ \bar{3}\ 4]_{\beta}$ and  $[4\ \bar{3}\ 3]_{\beta}$  poles and that with increasing beta stabilizing agent in this case molybdenum there is continuous change in the orientation of the habit plane as shown in Figure 15. This finding is a result of the continuous change in crystal structure from alpha prime martensite to alpha double prime martensite with increasing beta-stabilizing element (31).



Figure 15. Calculated habit plane normals for Ti-Mo alloy martensites, Mukherjee and Kato (5).

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## **CHAPTER 3**

### EXPERIMENTAL DESIGN AND PROCEDURE

# 3.1 Heat Treating of Ti 6211

## 3.1.1 Selection of Test Conditions

Preliminary heat treatment showed that, with the heat treating equipment, 30-35 minutes was adequate for solution treatment at the upper furnace. Longer time intervals were chosen to ensure equilibrium at the various isothermal annealing temperatures.

An argon atmosphere and pure titanium getters were used to minimize adsorption of interstial elements like hydrogen and oxygen in the alloy.

### 3.1.2 Procedure

The as-received sample plate was cut into small rectangular blocks  $(5 \times 2 \times 2)$  cm<sup>3</sup> and polished in 120 grade abrasive to remove blade marks and flatten the surface. More polishing was done through 600 grit before the sample was hot-worked.

The slight hotworking operation was done at about  $1090^{\circ}C$  and the samples were aircooled. The hotworked metal was profusely polished to remove any alpha case and oxidized layer. The clean samples of final dimension  $(3 \times 1 \times 1)cm^3$  were subsequently polished to 600 grit and then heat treated in a two-zone coaxial furnace assembly circulated with argon gas.

The furnace assembly was designed, as shown in Figure 16, to avoid contamination and ensure very rapid quenching rate.

The sample was solution treated in the upper furnace for about 35 minutes at around  $1030^{\circ}$ C and step-quenched to the lower furnace which was separately controlled. The equilibrium temperature on the sample was measured by means of a potentiometer and a digital millivoltmeter which was used to monitor temperature.

### 3.2 Analysis of the Heat Treated Samples

### 3.2.1 Optical Microscopy

This technique was used to study the variation of microstructure at various times and temperatures. An Olympus Table Microscope was used to have a quick glance on the samples but photomicrographs were taken with a Heerbrugg Wild Microscope Model M20 with attached 35 mm camera.

### 3.2.2 X-ray Diffraction

X-ray diffraction were performed on all the heat treated samples to identify the phases and index the planes.  $CuK_{\alpha}$  radiation was used at 20 KV and 15 ma.

### 3.2.3 Electron Microprobe Analyzer

This technique was used to determine the elemental distribution of the various microstructures in the heat treated samples. Working conditions were 20 KV and 10nA. Beam diameter was  $\approx 1000A^{\circ}$ . AlK $_{\alpha}$ , TaL $_{\alpha}$ , NbL $_{\alpha}$  and MoL $_{\alpha}$  wavelengths were used.



Figure 16. Heat treating equipment.
#### 3.3 Specimen Preparation

## 3.3.1 Optical Microscopy

Each heat treated sample was ground flat and any trace of oxide or coloration removed with the water-cooled Buehler Belt Surfacer. Rough polishing was done on 240, 320, 400, 600 emery papers adequately cooled to avoid deformation. Final polishing was done on the polishing wheel with microcloth using 0.05 micron alumina. The sample was etched for 40 seconds in 95 cc  $H_2O$ , 3.5 cc  $HNO_3$  and 1.5 cc HF, (Kroll's Etchant) and washed in water and then methanol and dried.

# 3.3.2 X-ray Diffraction

The size and shape of the sample necessitated the design of a special glass sample carrier into which the sample was placed with the samples' surface on the same level with surface of the glass sample carrier. Each sample prepared for the Optical Microscopy was repolished on a rotating wheel with cloth using 0.05 micron alumina and then etched slightly (15 seconds) in 95 cc  $H_2O$ , 3.5 cc  $HNO_3$  and 1.5 cc HF. (Kroll's Etchant).

### 3.3.3 Electron Microprobe Analyzer

The samples for the Probe analysis were prepared as for the x-ray diffraction.

# 3.4 Instrumental and Experimental Limitations (Situational)

### 3.4.1 Heat Treating

Titanium alloys are reactive at high temperatures to elements like oxygen and hydrogen. Hence as soon as the sample was introduced into the furnance, the furnace was flushed with argon gas and a continuous slow flow of argon gas was maintained with the aid of a flowmeter. This

flow was normally interrupted during the quenching operation. At this time of quenching some air must have unavoidably rushed into the furnace. However, it was hoped that this exposure was much shorter compared with the annealing time.

Quenching in water has its disadvantage. There was spontaneous nucleate boiling and decoloration of the sample at the instant of quenching. This decoloration was due to the spontaneous reaction between the hot metal and water. This decoloration was, however, removed during grinding.

## 3.4.2 ARL Electron Microprobe Analyzer

The best attainable beam diameter of the microprobe was 1000A<sup>0</sup>. Good beam diameter was, however, produced with high voltage and low current; hence, in this project 20 KV and 10nA were maintained constant in all the microanalysis. This 20 KV was just good enough to give reasonable counts. To reduce statistical error in the count rates, each spot count was for 1 minute. More than five count rates were recorded for each spot and the mean count rate was taken. The detector in the equipment saturates between 10,000 - 15,000 counts per second.

Quantitative microprobe analysis was not done in this project. Solute partitioning tendencies were studied qualitatively in the form of concentration profiles and concentration of various solutes in the various microstructures was measured in count rates. It is assumed that these raw data will reflect the concentration of each solute in the microstructures.

The current of 10nA was maintained constant, but it sometimes varied slightly. On the standard carrier, pure elements (standards) were embedded with other elements; for example, aluminum was embedded with cobalt. The possibility of interference of cobalt atoms in the emitted Al radiation may not be ruled out.

#### CHAPTER 4

## EXPERIMENTAL RESULTS

After the solution treatment and annealing of Ti 6211 at various temperatures, x-ray diffraction technique was used to identify the stable phases at each temperature after 48 hours annealing time.

Detailed analysis of the x-ray results was conducted. The detailed analyses are shown in the Appendix while the summaries are presented in Tables 10 to 16.

Based on the sample annealed at  $700^{\circ}$ C for 48 hours and quenched in water, average values of the lattice parameters for the HCP phase are calculated to be

$$a_{\alpha} = 2.938A^{\circ}$$
  
 $c_{\alpha} = 4.670A^{\circ}$ 

Similarly the lattice parameters for the BCC and orthorhombic phases were calculated from the samples annealed for 48 hours at  $800^{\circ}$ C and  $500^{\circ}$ C respectively and quenched in water. These lattice parameters are for the beta phase

 $a_{a} = 3.225 A^{0}$ 

and for the orthorhombic phase

$$a_{\alpha''} = 3.040 \text{Å}$$
  
 $b_{\alpha''} = 4.944 \text{\AA}$   
 $c_{\alpha''} = 4.637 \text{\AA}$ 

Based on these lattice parameters a complete set of allowed reflections for the hcp and BCC phases were calculated. This was calculated using CuKa radiation. The results of these calculations are summarized in Table 6 to 9 with increasing 20 angles.

A typical X-ray diffraction pattern for Ti 6211 annealed at  $500^{\circ}$ C,  $600^{\circ}$ C,  $700^{\circ}$ C,  $800^{\circ}$ C and  $900^{\circ}$ C for 48 hours in argon atmosphere is shown in Figure 17. It is not possible to distinguish between the  $\alpha_{0}$  and  $\alpha'$  in the x-ray diffraction work alone since they have the same crystal structure and very nearly the same lattice parameters. Thus all the hcp reflections in this study are designated alpha.

Optical microscopy of the as-received and the heat treated samples were performed to show morphological features. Figure 18 shows the optical micrograph of the as-received sample. The type fine  $\alpha + \beta$  colonies are observable. Figure 19 shows the optical micrograph of beta-solution treated, held for 30 minutes at various temperature and quenched in water at room temperature. The grain interior alpha and the packets of lath martensite are observable. More comments on this microstructure are included in the discussion.

Typical alpha-colony and basketweave microstructures in Ti 6211 obtained in samples annealed at  $600^{\circ}$ C,  $500^{\circ}$ C and  $400^{\circ}$ C and quenched in water are shown in Figure 20 A,B,C, respectively. Figure 21 A,B,C and D shows the samples annealed at  $500^{\circ}$ C,  $600^{\circ}$ C,  $700^{\circ}$ C and  $800^{\circ}$ C for 48 hours and quenched in water. The coarsening of alpha plates is observable. At higher temperatures this coarsening produces more equiaxed structure.

- Table 6: Possible reflections of HCP phases  $(\alpha, \alpha')$  in Ti 6211. Data taken from the sample annealed for 48 hours in argon atmosphere at 700°C and quenched in water at room temperature; with CuK $\alpha$ radiation.
  - $a = 2.9378 \stackrel{0}{A}$
  - c = 4.6697 Å

НСР		2θ (in deg.) (CuK <sub>α</sub> )*		
hkil	dhk1	λ	λ٦	λ2
1010	2.544	35.279	35.249	35.340
0002	2.334	38.573	38.540	38.640
1011	2.234	40.373	40.339	40.443
1012	1.720	53.257	53.210	53.352
1120	1.468	63.356	63.298	63.473
10 <b>1</b> 3	1.327	71.966	70,966	71.170
2020	1.272	74.611	74.539	74.756
1122	1.243	76.662	76.587	76.812
2021	1.227	77.849	77.772 -	78.002
0004	1.167	82.691	82.607	82.858
2022	1.117	87.287	87.196	87.468
10 <b>14</b>	1.061	93.203	93.103	93.404
20 <b>23</b>	0.985	103.009	102.890	102.248
2130	0.961	106.682	106.555	106.937
2131	0.941	110.020	109.889	110.292
1124	0.913	115.211	115.061	115.510

\*  $\lambda$  = Weighted average of the wavelengths of an unresolved K doublet of Cu radiation.

- $\lambda_1$  = Wavelength of CuK $\alpha_1$  radiation
- $\lambda_2$  = Wavelength of CuK<sub>a2</sub> radiation.

Table 7: Possible reflections of orthorhombic  $(\alpha^{"})$  phase in Ti 6211. Data taken from the sample annealed for 48 hours in argon atmosphere at 500°C and quenched in water at room temperature, using CuKa radiation.

Atom positions (0,0,0), (1/2,1/2,0),

(1/2, 1/6, 1/2), (0, 2/3, 1/2).

 $a = 3.040 \stackrel{o}{A}$ b = 4.944  $\stackrel{o}{A}$ 

c = 4.637 Å

 $2\theta$  (in deg.) (CuK<sub>2</sub>) hk1 dhk1 λ λ1 λ2 110 2.5896 34.647 34.617 34.706 020 2.472 36.342 36.311 36.405 002 2.318 38.850 38.817 38.917 111 2.261 39.871 39.836 39.940 021 2.181 41.399 41.363 41.471 112 1.727 53.024 52.977 53.119 022 1.691 54.245 54.196 54.342 200 1.520 60.952 60.897 60.046 130 1.449 64.286 64.226 64.405 113 1.327 71.034 70.966 71.170 220 1.295 73.068 72.998 73.209 023 1.310 72.099 72.030 72.237 202 1.271 74.680 74.607 74.825 221 1.247 76.372 76.297 76.521 040 1.236 77.176 77.101 77.328 004 1.159 83.389 83.303 83.558 222 1.130 86.036 85.947 86.213 1.058 93.749 114 93.547 93.446 024 1.049 94.598 94.496 94.804 0.99269 101.899 101.783 102.133 310 223 0.99256 101.918 101.801 102.152 0.9707 311 105.157 105.033 105.405 107.020 106.892 240 0.9589 107.277 330 0.8632 126.529 126.341 126.907 0.8352 134.747 135.205 313 134.520

Table 8:	Possible reflection of the BCC (β-phase) in Ti 6211. Calcu-
	lation based on various lattice parameters (0.02 Å steps) using
	cuka radiation.

a <sub>o</sub> = 3.21 Å			29 (in deg.) (CuK <sub><math>\alpha</math></sub> )		
	hk1	dnk1	λ	λ٦	λ2
	110	2.2698	39.710	39.675	39.778
	200	1.6050	57.413	57.361	57.516
	211	1.3104	72.074	72.005	72.212
	220	1.1349	85.575	85.487	85.751
	310	1.0151	98.831	98.721	99.053
	222	0.9266	112.606	112.464	112.891
	321	0.8579	127.952	127.758	127.342
a <sub>0</sub> = 3.23	110	2.2839	<b>39.454</b>	39.420	39.522
	200	1.6150	<b>57.024</b>	56.973	57.127
	211	1.3186	<b>71.556</b>	71.488	71.693
	220	1.1419	<b>84.926</b>	84.840	95.100
	310	1.0214	98.010	97.900	98.228
	222	0.9324	111.545	111.405	111.824
	321	0.8632	126.529	126.341	126.907
a <sub>o</sub> = 3.25	110	2.2981	39.200	39.167	39.268
	200	1.6250	56.642	56.591	56.741
	211	1.3268	71.046	70.979	71.182
	220	1.1490	84.280	84.194	84.45
	310	1.0277	97.205	97.097	97.42
	222	0.9382	110.510	110.374	110.78
a <sub>0</sub> = 3.27	321	0.8685	125.157	124.974	125.52
	110	2.3112	38.969	38.936	39.036
	200	1.6350	56.264	56.214	56.366
	211	1.3349	70.551	70.484	70.685
	220	1.1561	83.645	83.560	83.815
	310	1.0340	96.416	96.310	96.628
	222	0.9439	109.516	109.385	109.788
	321	0.8739	123.807	123.630	124.164

Table 9: Possible reflections of the BCC ( $\beta$ -phase) in Ti 6211. Data taken from the sample annealed 48 hours in argon atmosphere of 800°C and quenched in water at room temperature QuKa radiation was used.

$a_0 = 3.225 \text{ Å}$			$2_{\theta}$ (in deg.) (CuK <sub>a</sub> )		
	hkl	dhk1	λ	λ].	λ2
	110	2.280	39.525	39.490	39.593
	200	1.612	57.140	57.089	57.244
	211	1.316	71.719	71.651	71.856
	220	1.140	85.101	85.014	85.276
	310	1.019	98.321	98.211	98.540
	222	0.930	111.981	111.840	112.262
	321	0.861	127.113	126.923	127.496

-

Peak#	20 (deg)	(hkl)or (hkil)	Phase Identification
1	35.38	(10 <b>1</b> 0)	α
2	28.51	(0002)	α
3	39.87	(111)	a"
4	40.21	(1011)	α
5	53.11	(1012)	α
6	63.30	(1120)	α
7	71.95	(1013), (113)	a, a"
8	74.56	(20 <b>20), (202</b> )	a, a"
9	76.45	(221), (1122)	a",a
10	77.57	(2021)	α
11	87.0	(20 <b>22)</b>	α
12	102.70	(20 <b>23</b> )	- α
13	111.95	(21 <b>3</b> 1)œ	α

Table 10: 20 angle for samples annealed at 500°C for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuKa radiation.\*

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\*For detailed analysis seed Table A-1 in the Appendix.

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Table 11: Experimental 20 angles for samples annealed at 600°C for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuKα radiation.\*

Peak#	2θ (deg)	(hkl) or (hkil)	Phase Identification
1	35.31	(1010)	α
2	38.60	(00 <b>02)</b> a	α
3	39.73	(111)a",	α"
4	40.28	(10 <b>T1)</b>	α
5	53.11	(112)a", (1012)a	α", α
6	63.23	(1120)	α
7	71.90	(10 <b>13)</b> a, (113)a"	a, a",
8	76.53	(1122), (221)	α, α"
9	77.73	(2021)	a
10	82.21	(0004)	a
11	85.50	(222)a"	α",
12	106.71	(2130)	a
13	111.90	(2131)	α
14	115.06	(1124)	α

\*For detailed analysis see Table A-2 in the Appendix.

Peak#	2 0 (deg)	(hkl) or (hkil)	Phase Identification
1	35.31	(10\0)	α
2	38.60	(0002)	α
3	39.53	(110)	β
4	40.34	(1011)	α
5	53.24	(1012)	α
6	63.30	(1120)	α
7	70.72	(10 <b>1</b> 3)	α
8	71.76	(211)	β
9	74.64	(2020)	α
10	76.61	(1122)	α
11	77.69	(2021)	α
12	82.45	(0004)	α
13	87.0	(20 <b>22</b> )	α
14	111.10	(21 <b>3</b> 1)α, (222)β	α, β

Table 12: Experimental 2Θ angles for samples annealed at 700°C for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuKα radiation.\*

\*For detailed analysis see Table A-3 in the Appendix.

Peak#	2 0 (đeg)	(hkl) or (hkil)	Phase Identification
1	35.38	(10 <b>T</b> 0)	α
2	38.58	(0002)	α
3	39.52	(110)	β
4	40.48	(10 <b>1</b> 1)	α
5	53.20	(10 <b>1</b> 2)	α
6	57.12	(200)	β
7	63.50	(1120)	α
8	71.0	(10 <b>13)</b> .	α
9	71.64	(211)	β
10	74.64	(20 <b>20)</b>	α
11	76.45	(1122)	α
12	77.77	(2021)	α
13	82.21	(0004)	α
14	84.53	(220)	β
15	86.85	(2022)	α
16	102.78	(2023)	α
17	106.19	(2130)	α
18	111.60	(21 <b>3</b> 1)a, (222)	β α, β

Table 13: Experimental 20 angles for samples annealed at 800°C for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuKa radiation.\*

\*For detailed analysis see Table A-4 in the Appendix.

Peak#	2 ð (deg)	(hkl) or (hkil)	Phase Identification
1	35.38	(10 <b>1</b> 0)	α
2	38.24	(0002)	α
3	39.51	(110)	β
4	40.14	(1011)	α
5	52.89	(10 <b>12)</b>	a
6	62 <b>.</b> 96	(1120)	α
7	71.60	(211)	β
8	74.64	(20 <b>20)</b>	α
9	76.46	(1122)	α
10	81.41	(0004)	α
11	85.00	(220)	в
12	106.25	(2130)	α
13	111.00	(21 <b>31)</b> a, (222)	β α, β

Table 14:	Experimental 20 angles for samples annealed at 900°C f	or
	48 hours in argon atmosphere and quenched in water. D	)ata
	taken at 22°C with CuKa radiation.*	

\*For detailed analysis see Table A-5 in the Appendix.

Peak#	20 (deg)	(hkl) or (hkil)	Phase Identification
1	35.31	(10 <b>1</b> 0)	α'
2	38.44	(0002)	α'
3	40.21	(10 <b>11</b> )	α'
4	53.15	(10 <b>12)</b>	α'
5	62.97	(1120)	α '
6	71.20	(10 <b>1</b> 3)	<b>α'</b>
7	74.16	(20 <b>20</b> )	α'
8	76.50	(1122)	α'
9	77.25	(2021)	α <sup>1</sup>
10	81.57	(0004)	α'
11	87.19	(2022)	α'
12	92.24	(10 <b>1</b> 4)	α'
13	102.25	(20 <b>23</b> )	α'

(2131)

α'

Table 15: Experimental 20 angles for samples annealed 30 minutes at 1070°C in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with  $CuK\alpha$  radiation.\*

\*For detailed analysis see Table A-6 in the Appendix.

110.00

14

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Peak#	20 (deg)	(hkl) or (hkil)	Phase Identification
1	35.30	(10โ0)	α
2	38.55	(0002)	α
3	39.60	(110)	β
4	40.35	(10 <b>1</b> 1)	α
5	53.15	(1012)	a
6	63.30	(1120)	α
7	71.70	(211)	β
8	74.60	(20 <b>20)</b>	α
9	76.52	(1122)	a
10	77.60	(2021)	α
11	82.20	(0004)	α
12	102.70	(2023)	α
13	106.02	(2130)	· a
14	110.00	(2131)	α
15	114.50	(1124)	α

Table 16: 20 values of the as-received Ti 6211 plate prior to heat treatment. Data taken at 22°C with CuKa radiation.\*

\*For detailed analysis see Table A-7 in the Appendix.

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Figure 17. Typical X-ray diffraction pattern for Ti 6211 annealed at 500°C, 600°C, 700°C, 800°C and 900°C for 48 hours and quenched in water.

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Figure 18. Optical micrograph of the as-received Ti 6211 showing fine alpha + beta colony microstructure. Etchant is Kroll's solution, magnification: 200X



Figure 19. Optical micrograph of Ti 6211 annealed 30 minutes at 1070<sup>0</sup>C, and 900<sup>0</sup>C and quenched in water at room temperature. Etchant is Kroll's solution, magnification: 200X.

- Figure 20: Typical alpha-colony and basketweave microstructure for Ti 6211. Etchant Kroll's solution.
  - A: Basketweave microstructure for sample annealed at  $400^{\circ}$ C and quenched in water at room temperature.
  - B: Alpha-colony microstructure for sample annealed at 500°C and quenched in water at room temperature.
  - C: Alpha-colony microstructure for sample annealed at 600°C and quenched in water at room temperature. Mag. for all = 150X



Figure 21. Optical Micrograph of Ti 6211 aged for 48 hours in argon atmosphere at 500°C, 600°C, 700°C, 800°C and quenched in water. Etchant: Krolls Solution (1.5HF, 3.5HNO<sub>3</sub>, 95H<sub>2</sub>0). Mag. for all = 200X



Scanning Electron Microscopy was also conducted to depict some features in the microstructure. Figure 22 shows the scanning electron image of the beta solution treated and subsequent 30 minutes annealing at 900<sup>°</sup>C and quenching in water. The martensite plates occurring as alpha prime plates, the retained beta and the alpha colony are observed.

Figure 22 also shows the heterogeneously nucleated grain boundary alpha. Figure 23 shows alpha blocks in the trijunction.

From the Electron Microprobe Analysis further characterization of Ti 6211 is conducted. Figure 24 shows the solute partitioning of aluminum in the sample annealed 90 minutes at 500<sup>0</sup>C and quenched in water. This profile is non-regular because of some inhomogeneities in the heat treated sample. This non-regularity is still observed at long annealing times as shown in Figure 25.

Figures 25 and 26 depict the mirror image partitioning of aluminum and tantalum. The aluminum partitions to the alpha-plate while Tantalum partitions to the beta-phase. The alpha-plate here has light colour while the beta-phase has the dark colour.



Figure 22. Scanning Electron Image of Ti 6211 annealed for 30 minutes at 900°C and quenched in water at room temperature. Etchant is Kroll's solution. Mag: 750X



Figure 23. Scanning Electron Image of Ti 6211 showing the alpha blocks in the trijunction. Etchant is Kroll's solution. Mag: 500X



Figure 24. Qualitative solute partitioning of aluminium in the sample annealed for 90 minutes at 500°C and quenched in water.



Figure 25: Solute partitioning of aluminium and tantalum in Ti 6211 annealed 20 hours at 500°C and quenched in water, showing mirror image partitioning tendency of Al and Ta.



Figure 26. Solute partitioning of aluminium and tantalum in Ti 6211 annealed 20 hours at 600°C and quenched in water showing mirror image partitioning of Al and Ta.

#### CHAPTER 5

#### DISCUSSION OF EXPERIMENTAL RESULTS

The objective of this research as stated in the abstract was achieved by solution-treating and annealing the samples in two coaxial furnaces circulated with argon gas, such that the sample was inside the furnace throughout the whole operation. Rapid quenching after annealing was ensured by burning a high resistance wire holding the sample and the sample dropping instantaneously into water at room temperature.

From subsequent analysis it was found that the phases that can be formed in Ti 6211 are  $\alpha_0$ ,  $\alpha'$ ,  $\alpha''$ , and  $\beta$ .  $\alpha_0$ ,  $\alpha'$  and the  $\beta$ (retained) were identified in the samples annealed at 900°C, 800°C and 700°C and quenched in water, with the beta decreasing in volume fraction as the temperature of annealing was lowered. For the samples annealed at  $600^{\circ}$ C and  $500^{\circ}$ C and quenched in water the phases identified were  $\alpha_0$  and  $\alpha''$ .

It has been shown (31) that when alpha double prime martensite formed the splitting of alpha-peaks occurred with increasing betastabilizing molybdenum content in Ti-Al. In our present alloy splitting was only observed at  $500^{\circ}$  and  $600^{\circ}$ C where alpha double prime was formed. However a systematic  $\beta$  peak shift at around  $39.51^{\circ}$ ,  $2\theta$  angle at  $900^{\circ}$ C to  $39.53^{\circ}$   $2\theta$  angles at  $700^{\circ}$ C was observed in the present study. This peak was identified as beta-phase at  $700^{\circ}$ C,  $800^{\circ}$ C and  $900^{\circ}$ C and as alpha double prime at  $500^{\circ}$ C and  $600^{\circ}$ C. The shifting was accompanied by very small

change in the beta-lattice parameter, which decreased as the annealing temperature was decreased. At  $500^{\circ}$ C the alpha double prime peak almost merged with the  $(10\overline{1})_{\alpha}$  line, Figure 17.

It must be noted that when a sample was annealed at  $1025^{\circ}C$  and then down-quenched to a lower temperature such as  $600^{\circ}C$  or  $500^{\circ}C$  the sample passed through the two phase  $\alpha + \beta$  region in a relatively short time. For example experimental studies indicated that the time required for the sample to come to an equilibrium at  $500^{\circ}C$  was about 10 minutes. Thus an equilibrium was not attained during the passage of the sample through the  $\alpha + \beta$  phase field. The sample at  $500^{\circ}$ ,  $600^{\circ}C$  and  $700^{\circ}C$  started with a non-equilibrium amounts of alpha and beta phases. If  $500^{\circ}C$  were below the alpha-solvus line, then conversion of the retained beta to the equilibrium alpha at this temperature would occur by diffusional decomposition of the beta-quenched-in at  $500^{\circ}C$ . The rate of diffusion at  $500^{\circ}C$ , however, is quite slow. The situation can be illustrated diagrammatically in Figure 27.

Further this decomposition involved diffusion of Al out of the beta-phase to nucleate the Al-rich equilibrium alpha-phase. Such nucleating regions must also reject the beta-stabilizing elements.

The regions that have a very high supersaturation of the beta stabilizers upon quenching will be trapped as retained beta between the the equilibrium alpha-laths. However, depending on the degree of this supersaturation the quenching could transform these regions to alpha prime or alpha double prime martensites. It has been shown (93) that a transition from alpha prime to alpha double prime martensite in titanium alloy occured as a function of increasing beta-stabilizing solutes.



Figure 27.  $\beta$ -transformation at 500°C.  $\alpha_{c} = Equilibrium \alpha$  that nucleated from the  $\beta$ -phase during  $\alpha_{c} = Equilibrium \alpha + \beta$  region.  $\alpha_{0}^{500} = Equilibrium \alpha$  at 500°C. From the present investigation since we observed alpha double prime martensite at  $500^{\circ}$ C and  $600^{\circ}$ C it can be concluded that such a mechanism was operating in this system.

In order to obtain a qualitative idea regarding the nature of the diffusion, we calculated the diffusion coefficients of aluminum in Ti-Al alloys in the beta phase. Using the data reported by K. Ouchi et al (94) Table 17 and 18 were constructed for various annealing temperatures and 48 hours annealing time.

Based on the data in Tables 17 and 18 it is clear that diffusion rates of aluminum in the beta-phase were much slower compared with the diffusion rates of aluminum in the alpha-phase. The proposed model of localized supersaturation of the beta-phase which transformed to alpha double prime on subsequent quenching could be justified from this difference in the diffusion rates. Additionally the low diffusion rate of aluminum in the alpha-phase, at low temperatures, would account for some inhomogeneities in the alpha-phase especially at short annealing times when the  $\alpha_c$  was not fully homogenized.

These inhomogeneities, due to the low diffusion rates, gave rise to the non-regularity (as seen in Figure 24) of the wavelength dispersive x-ray solute partitioning profiles, especially at short times of annealing. At long times such non-regularity was still observed (see Figure 25) but the occurrence depended on the size of the alpha-plates and beta-films. The alpha-plate was about two microns and the beta-region was less than one micron depending, however, on the annealing temperature.

Temperature,K	D <sub>o</sub> x10 <sup>-6</sup>	Q kJ/mol.	D(m <sup>2</sup> /sec) in β-phase	Average diffusion distance $\bar{x} = (Dt)^{\frac{1}{2}}$ in microns 48 hours annealing time
773	2.90	180	$2.0 \times 10^{-18}$	~ 0.6
873	2.90	180	5.0 $\times 10^{-17}$	~ 3
973	2.90	180	$6.0 \times 10^{-16}$	~ 10
1073	2.90	180	5.0 x 10 <sup>-15</sup>	~ 29
1173	2.90	180	$28.0 \times 10^{-15}$	~ 69

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Table 17. Calculated diffusion data for aluminium in beta-phase for Ti-4.55w/oAl.
Тетр К	D <sub>o</sub> x 10 <sup>-13</sup>	Q KJ	D m <sup>2</sup> /sec in α-phase	Average diffusion distance $\bar{x} = (Dt)^{\frac{1}{2}}$ in microns 48 hours annealing time
773	8.70	70.7	$1.0 \times 10^{-17}$	~ 1.5
873	8.70	70.7	5.0 $\times .10^{-17}$	~ 3
973	8.70	70.7	1.0 x 10 <sup>-16</sup>	~ 5
1073	8.70	70.7	$3.0 \times 10^{-16}$	~ 7
1173	8.70	70.7	6.0 x 10 <sup>-16</sup>	~10

Table 18. Calculated diffusion data for aluminium in the alpha-phase for Ti-4.lw/oAl alloy.

The solute partitioning tendencies of tantalum a beta-stabilizer, and aluminum an alpha stabilizer further confirmed the model of localized supersaturation in the beta-phase and the occurrence of inhomogeneities in the alpha-phase. The overall observation, however, was that tantalum partitioned to the inter alpha regions which were the beta-regions at elevated temperatures. Aluminum on the other hand partitioned to the alpha plates both on the grain boundary when the grain boundary alpha formed and in the grain itself. The partitioning tendencies of tantalum and aluminum were mirror images to each other, see Figures 25,26. This trend was clearly observable at low temperatures and long annealing times. The occurrence of supersaturated regions was further confirmed by occasional high peaks and deep troughs in the solute partitioning profiles. Figures 25 and 26 show the partitioning of tantalum and aluminum at  $500^{\circ}$ C and 600°C after 20 hours annealing and quenching. The aluminum rich regions corresponded to the alpha-plates and the aluminum poor regions which were tantalum rich regions corresponded to the inter-alpha regions which were either beta-phase or alpha double prime depending on the annealing temperature. This stems from the obvious fact that tantalum and other beta stabilizers dissolve preferrentially in the beta-phase and aluminum and other alpha-stabilizers dissolve preferrentially in the alpha-phase.

Considering the binary phase diagrams Figure 4, 5, 6, and 7 after Hansen et al (95,96) it is observed that the beta stabilizers, namely Nb, Ta and Mo lower the  $\alpha/\alpha + \beta$  solvus line. The overall effect of these elements to Ti-Al system is speculative.

Recently Shull et al (97) showed the phase diagram for Ti-Mo-Al alloy system, Figure 28, in which the effect of 0.5 a/o Mo on Ti-Al



Figure 28. Ti-Al phase diagram showing effect of 0.50 a/o Mo on Ti-Al binary system. Thin background lines indicate the diagram for Ti-Al system, after Shull et al (97).

binary system is the slight lowering of both the  $\alpha/\alpha + \beta$  and  $\alpha + \beta/\beta$ phase boundaries. It is likely that the  $\alpha/\alpha + \beta$  and  $\alpha + \beta/\beta$  phase boundaries are further lowered with accompanying widening of the  $\alpha + \beta$ phase field.

There is also the possibility that at lower annealing temperatures, Ti 6211 may have  $\alpha_2$  an order DO<sub>19</sub>, Ti<sub>3</sub>Al phase (97). This possibility was examined based on the x-ray diffraction results.

The position of fundamental diffraction peaks of  $\alpha_2$ -phase was almost identical to those of the alpha-lines (98). In addition supperlattice peaks from the ordered DO<sub>19</sub> structure should appear. But in the present investigation all x-ray diffraction lines were accounted for as  $\alpha$ ,  $\beta$  or  $\alpha$ " and there were no extra lines which could be identified as the supperlattice reflections. Thus either the volume percent of  $\alpha_2$ phase in this alloy was below the limit of detection by x-ray diffraction or the occurrence of  $\alpha_2$  could be ruled out for the annealing times and/or temperatures of the present study.

It has been pointed out by Margolin et al (99) that with an increasing amount of beta-stabilizer in the beta-phase the independent nucleation of separate plates was enhanced and the colony microstructure was replaced by the basketweave or the widmanstatten microstructure. Typical alpha colony microstructure at  $600^{\circ}$ C and the basketweave at  $500^{\circ}$ C for Ti 6211 are shown in Figure 21.

These microstructures further confirm that the beta stabilizers in the equilibrium beta increased as annealing temperature was lowered.

Further morphological information was obtained from the scanning electron microscopy. Figure 22 shows the electron image of a sample aged

for 30 minutes at  $900^{\circ}$ C and quenched in water. The martensitic plates occurring as alpha prime plates, the retained beta and the alpha colony are observable.

The heterogeneous nucleation of alpha on the prior beta-grain boundary is shown in the scanning electron micrograph, Figure 23. This alpha-plate nucleated and grew along the grain boundary to form a continuous grain boundary alpha.

From the electron microprobe analysis it appeared that the aluminum content of the grain boundary alpha was slightly smaller than the Aluminium content of alpha-colony. The pattern of the various alpha colonies was noteworthy. The alpha colony terminating at the grain boundary alpha showing that the two alpha microstructures must have nucleated differently.

At high annealing temperatures, such as 900°C or 800°C, a heterogeneous nucleation of equilibrium alpha phase occured at the prior beta grain boundaries. As these grain boundary alpha grew there was a depletion of Al (and thus a supersaturation of beta-stabilizers) adjacent to the grain boundaries. The grain interior, however, did not suffer such an Al depletion. Thus simultaneously or concurrently equilibrium alpha-colonies formed at the grain interior. The remaining matrix, after the isothermal heat-treatment, consisted of beta-phase. Among the retained beta regions, the volume adjacent to a grain boundary was the most supersaturated beta because of the higher diffusion rate of solutes near the boundary. Upon quenching, the beta-phase transformed martensitically giving rise to a "packet" type martensitic structure. The retained beta near the grain boundaries, however, was supersaturated with beta-stabilizers to such a degree that upon cooling or quenching

to room-temperature, it was retained. The x-ray data confirmed the existence of the beta-phase in alloys quenched from  $800^{\circ}$ C and  $900^{\circ}$ C. The scanning electron and optical micrographs, Figure 22 and Figure 23, show the nature of equilibrium alpha colonies, grain interior, packet martensites, and the structureless zone (enriched beta-phase) between the grain boundary alpha and the martensitic packets. Schematically this situation is explained in Figure 29.

Further it is appropriate to make few remarks about the phenomenological theories as well as the strain energy minimization criterion mentioned in this research. Both tacitly assume the uniform distribution of transformation strain and lattice invariant shear. It is true that using these phenomenological analysis one can obtain the situation where the elastic strain energy is zero. If this theory is accepted the supercooling phenomenon which characterizes the martensitic transformation should not be observed because there would be no factors opposing the transformation.

Thus in order to understand the energetics of martensitic transformation it is essential to take into account the actual periodic distribution of transformation strains and lattice invariant shear as has been done by Mura et al (4) and Kato et al (89).



Figure 29. Schematic illustration of the microstructures for samples annealed for short times at 800°C and 900°C and quenched in water at room temperature.

## CHAPTER 6

### SUMMARY AND CONCLUSION

In this research fundamental principles were used to characterize the phase transformations in this complex quartenary Ti alloy and the following conclusions are made.

1. The x-ray diffraction experiments showed that  $\alpha_0$ ,  $\alpha'$ ,  $\alpha''$ ,  $\alpha''$ , and  $\beta$  phases could be obtained in Ti 6211 after isothermal and quenching heat treatments. Specifically at higher temperatures 700°C, 800°C, and 900°C  $\alpha_0$ ,  $\alpha'$  and retained  $\beta$  were stable, at lower temperatures  $\alpha_0$ ,  $\alpha''$  phases were stable. The existence of  $\alpha_2$  (Ti<sub>3</sub>Al) in this system in the prescribed heat treatments was not confirmed because of the absence of the extra superlattice peaks from  $\alpha_2$ , DO<sub>19</sub> structure. This absence might result from very small volume fraction of  $\alpha_2$  in this alloy.

The splitting of  $\alpha$ -peaks to satelite orthorhombic peaks is not observed in this system, at high temperatures where  $\alpha$ " was not obtained on quenching. At 500<sup>0</sup> and 600<sup>0</sup>C where  $\alpha$ " was obtained, splitting occurred.

2. The lattice parameters of the prevalent phases in Ti 6211 are found as follows:

 $\beta$ -phase:  $a_{\beta} = 3.225 \text{\AA}$ 

 $\alpha-phase:$   $a_{\alpha} = 2.938 \overset{O}{A}$   $c_{\alpha} = 4.670 \overset{O}{A}$ Orthorhombic:  $a_{\alpha''} = 3.040 \overset{O}{A}$   $b_{\alpha''} = 4.944 \overset{O}{A}$   $c_{\alpha''} = 4.637 \overset{O}{A}$ 

Slight variation of these parameters at various temperatures was observed.

3. The Electron Microprobe Analysis showed qualitatively that aluminum has strong partitioning in the alpha regions and the grain boundary alpha (Gba). Tantalum exhibited weak partitioning to beta, alpha prime and alpha double prime regions. This was expected as alpha prime and alpha double prime came from the high temperature beta phase on quenching. Aluminum and tantalum partitioning occurred in mirror image to each other especially at low temperatures.

4. Based on the phases identified in quenched alloys and the solute diffusion model proposed in this study, tentative  $\alpha$  and  $\alpha + \beta$  phase boundaries are schematically shown in Figure 30.

Our proposed phase boundaries are in qualitative agreement with those proposed by Shull et al (97) for a ternary Ti-Mo-AL alloy. We believe, however, that due to the additional  $\beta$ -stabilizers, namely Ta and Nb, 900<sup>O</sup>C and 800<sup>O</sup>C are also within the  $\alpha + \beta$  phase field.

Further our results as well as Shull's et al results, indicate that the phase equilibria proposed by Williams (2) wherein  $500^{\circ}$ C to  $900^{\circ}$ C are all in two phase  $\alpha + \beta$  region is incorrect.



Figure 30. Schematic  $\alpha$  and  $\alpha + \beta$  phase boundaries in Ti 6211 alloy based on quenched structures.

5. We have observed a continuous, heterogeneously nucleated grain boundary  $\alpha$ -phase at higher annealing temperatures and relatively long annealing times. From the tentative phase boundaries it is apparent that the two phase  $\alpha + \beta$  region for Ti 6211 alloy extends over a relatively narrow temperature range that is ~ 950°C to ~ 800°C. Thus the "nose" of the isothermal T-T-T diagram, for equilibrium  $\alpha + \beta$  phase separation lies between 950°C and 800°C. The nature and extent of grain boundary  $\alpha$  formation, therefore, depends on the annealing temperature within the  $\alpha + \beta$ phase field. An extensive grain boundary  $\alpha$  and an associated soluterich retained  $\beta$  near the grain boundary, might have an adverse effect on the fracture properties of this alloy. It must be pointed out that a ductility dip for this alloy has been observed (2) at about 850°C. Whether this ductility loss is related to such a microstructural change must be investigated by future experimentation.

6. Further microchemical and structural studies must be conducted to obtain a quantitative phase diagram. It will be necessary to conduct simultaneous microdiffraction and chemical analysis using high resolution STEM. Such an experiment is planned for the near future.

7. Using the analysis of Mukherjee and Kato (5) the crystallographic aspects of  $\alpha'$  and  $\alpha''$  martensites could be computed. However, no experimental results exist for the habit plane(s) for the martensites in this alloy. Thus an experimental determination of the habit plane is planned. This study will include high resolution TEM and micro-micro diffraction. It must also be pointed out that very little is known about the internal structure of the martensite in this class of alloys. An attempt should, therefore, be made to investigate the nature of the lattice invariant shear for these martensitic transformations.

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# APPENDICES

Peak #	hkl or hkil	20 Expt.	20 Calc.	CuKa
1	(10 <b>1</b> 0)α	35.38	35.28	λ
2	(002)a (002)a"	38.51 38.51	38.57 38.85	λ λ
3	(111)α" (110)β	39.87 39.87	39.87 39.71	λ λ
4	(1011)a (021)a"	40.21 40.21	40.37 41.40	λ λ
5	(1012)a (112)a"	53.11 53.11	53.25 53.02	λ λ
6	(1120)a	63.30	63.35	λ
7	(10]3)α (113)α" (211)β	71.95 71.95 71.95	71.03 71.03 72.07	λ λ λ
8	(2020)a (202)a''	74,56 74.56	74.61 74.68	λ λ
9	(1122)a	76.45	76.66	λ
	(221)a"	76.45	76.38 76.29	$\lambda_1$ $\lambda$ $\lambda_1$
10	(2021)a	77.57	77.85	λ
	(040)a"	77.57	77.17 77.10	$\lambda_{1}$ $\lambda_{1}$
11	(2022)a	87.0	87.28	λ
	(222)a"	87.0	86.03 85.95	$\lambda_1$ $\lambda_1$
12	(2023)a	102.70	102.89	λ
13	(21 <b>3</b> 1)α (222)β	111.95 111.95	109.88 112.46	$\lambda_1 \\ \lambda_1$

<u>APPENDIX I</u>: Table A-1. Structural analysis of Ti 6211 annealed at  $500^{\circ}$ C for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuK<sub>a</sub> radiation.

 $\begin{array}{c} \underline{\text{APPENDIX II}:}\\ \hline \text{Table A-2.}\\ \hline \text{Structural analysis of Ti 6211 annealed at 600}^{O}\text{C for 48}\\ \hline \text{hours in argon atmosphere and quenched in water at room}\\ \hline \text{temperature.}\\ \hline \text{Data taken at 22}^{O}\text{C with } \text{CuK}_{\alpha} \text{ radiation.} \end{array}$ 

Peak #	hkl or hkil	20 expt.	20 calc.	CuK
1	(10 <b>1</b> 0)∝	35.31	35.28	λ
2	(0002)a (002)a"	38.60 38.60	38.57 38.85	λ λ
3	(111)α" (110)β	39.73 39.73	39.87 39.52	λ λ
4	(10 <b>1</b> 1)a (021)a"	40.28 40.28	40.37 41.40	λ λ
5	(112)a" (1012)a	53.11 53.11	53.02 53.25	λ λ
6	(1120)a	63.23	63.35	λ
7	(10 <b>1</b> 3)α (113)α" (211)β	71.90 71.90 71.90	71.03 71.03 72.00	λ λ λ
8	(1122)a (221)a"	76.53 76.53	76.66 76.58 76.37 76.29	$\lambda \\ \lambda_1 \\ \lambda \\ \lambda_1 \\ \lambda_1$
9	(2021)a (040)a″	77.73 77.73	77.85 77.77 77.17 77.10	λ λ 1 λ λ
10	(0004)a	82.21	82.60 82.86	λ λ
11	(220)β (222)α"	85.50 85.50	85.49 85.95	$\lambda_1 \\ \lambda$
12	(2130)a (240)a"	106.71 106.71	106.55 106.89	$\lambda \lambda_1$
13	(21 <b>3</b> 1)α (222)β	111.90 111.90	109.88 112.46	$\lambda_1 \\ \lambda_1$
14	(1124)α	114.27	115.06	$\lambda_1$

APPENDIX II	I:
Table A-3.	Structural analysis of Ti 6211 annealed at 700 <sup>0</sup> C for 48
	hours in argon atmosphere and quenched in water. Data
	taken at 22°C with CuKa radiation.

Peak #hkl or hkil20 expt.20 calc.1 $(10^{1}0)\alpha$ 35.3135.282 $(0002)\alpha^{"}$ 38.6038.853 $(111)\alpha^{"}$ 39.5339.873 $(111)\alpha^{"}$ 39.5339.824 $(10^{1}1)\alpha^{"}$ 40.3440.375 $(10^{1}2)\alpha^{"}$ 53.2453.256 $(112)\alpha^{"}$ 53.2453.026 $(112)\alpha^{"}$ 63.3063.357 $(10^{1}3)\alpha^{"}$ 70.7271.03 $(113)\alpha^{"}$ 70.7271.038 $(211)\beta$ 71.7571.72a = 3.2259 $(2020)\alpha^{"}$ 74.6474.61 $(202)\alpha^{"}$ 76.6176.68 $(221)\alpha^{"}$ 76.6176.68 $(221)\alpha^{"}$ 77.6977.85 $(11)$ $(2021)\alpha^{"}$ 77.6911 $(2021)\alpha^{"}$ 76.37 $(2022)\alpha^{"}$ 8787.2813 $(2022)\alpha^{"}$ 878 $(211)\beta\alpha^{"}$ 8714 $(2131)\alpha^{"}$ 111.10100.8895		
1 $(10\overline{1}0)_{\alpha}$ 35.3135.282 $(002)_{\alpha}^{"}$ 38.6038.573 $(111)_{\alpha}^{"}$ 39.5339.873 $(111)_{\alpha}^{"}$ 39.5339.874 $(10\overline{1}1)_{\alpha}^{"}$ 40.3440.375 $(10\overline{1}2)_{\alpha}^{"}$ 53.2453.256 $(11\overline{2}0)_{\alpha}^{"}$ 63.3063.357 $(10\overline{1}3)_{\alpha}^{"}$ 70.7271.038 $(211)_{\beta}$ 71.7571.72 a = 3.2259 $(20\overline{2}0)_{\alpha}^{"}$ 74.6474.61 $(202)_{\alpha}^{"}$ 76.6176.66 $76.29$ $(20\overline{2}1)_{\alpha}$ 77.6911 $(20\overline{2}1)_{\alpha}^{"}$ 77.6977.85 $(040)_{\alpha}^{"}$ 77.6976.2912 $(0004)$ 82.4582.6013 $(20\overline{2}2)_{\alpha}^{"}$ 8787.2814 $(21\overline{3}1)_{\alpha}$ 111.10109.88	eak #	<u>CuKa</u>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	λ
3 $(111)_{\alpha}^{"}$ 39.53       39.87         4 $(10\overline{1}1)_{\alpha}^{"}$ 40.34       40.37         5 $(10\overline{1}2)_{\alpha}^{"}$ 53.24       53.25         6 $(11\overline{2}0)_{\alpha}^{"}$ 63.30       63.35         7 $(10\overline{1}3)_{\alpha}^{"}$ 70.72       71.03         8 $(211)_{\beta}$ 71.75       71.72 a = 3.225         9 $(20\overline{2}0)_{\alpha}$ 74.64       74.61         74.64       74.64       74.68         10 $(11\overline{2}2)_{\alpha}$ 76.61       76.68 $(202)_{\alpha}^{"}$ 76.61       76.58 $(213)_{\alpha}^{"}$ 77.69       77.85 $(20\overline{2}1)_{\alpha}$ 77.69       77.85 $(20\overline{2}1)_{\alpha}^{"}$ 76.61       76.37 $(20\overline{2}1)_{\alpha}^{"}$ 77.69       77.85 $(20\overline{2}1)_{\alpha}^{"}$ 77.69       77.85 $(11)_{\alpha}^{"}$ 77.69       76.37 $(2000)_{\alpha}^{"}$ 82.45       82.60 $(213)_{\alpha}^{"}$ 87       87.28 $(213)_{\alpha}^{"}$ 87       87.28 $(213)_{\alpha}^{"}$ 87       86.03 $(213)_{\alpha}^{"}$	2	λ λ
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3	λ 25 λ
5 $(10\bar{1}2)_{\alpha}$ 53.2453.256 $(11\bar{2}0)_{\alpha}$ 63.3063.357 $(10\bar{1}3)_{\alpha}$ 70.7271.038 $(211)_{\beta}$ 71.7571.72 a = 3.2259 $(20\bar{2}0)_{\alpha}$ 74.6474.61 $(202)_{\alpha}$ 74.6474.6810 $(11\bar{2}2)_{\alpha}$ 76.61 $(21)_{\alpha}$ 76.6176.58 $(21)_{\alpha}$ 77.6977.85 $(21)_{\alpha}$ 77.6977.85 $(21)_{\alpha}$ 77.6976.37 $(20\bar{2}1)_{\alpha}$ 77.6976.37 $(20\bar{2}2)_{\alpha}$ 8782.8613 $(20\bar{2}2)_{\alpha}$ 8787.28 $(222)_{\alpha}$ 8787.19 $(222)_{\alpha}$ 8785.9514 $(21\bar{3}1)_{\alpha}$ 111.10109.88	4	λ λ
6 $(11\overline{2}0)_{\alpha}$ 63.30       63.35         7 $(10\overline{1}3)_{\alpha}$ 70.72       71.03         8 $(211)_{\beta}$ 71.75       71.72 a = 3.225         9 $(20\overline{2}0)_{\alpha}$ 74.64       74.61         9 $(20\overline{2}0)_{\alpha}$ 74.64       74.68         10 $(11\overline{2}2)_{\alpha}$ 76.61       76.66         76.29       71.75       77.69       77.85         11 $(20\overline{2}1)_{\alpha}$ 77.69       77.85         11 $(20\overline{2}1)_{\alpha}$ 77.69       77.85         12 $(0004)$ 82.45       82.60         13 $(20\overline{2}2)_{\alpha}$ 87       87.28         14 $(21\overline{3}1)_{\alpha}$ 111.10       109.88       6.03	5	λ λ
7 $(10\bar{1}3)_{\alpha}^{\alpha}$ 70.72 70.72+71.03 71.038 $(211)_{\beta}$ 71.7571.72 a = 3.2259 $(20\bar{2}0)_{\alpha}^{\alpha}$ 74.64 74.6474.61 74.6810 $(11\bar{2}2)_{\alpha}^{\alpha}$ 76.61 76.6176.66 76.58 76.2911 $(20\bar{2}1)_{\alpha}^{\alpha}$ 77.69 77.6977.85 77.77 76.2912 $(0004)$ 82.45 82.60 82.8613 $(20\bar{2}2)_{\alpha}^{\alpha}$ 87 	6	λ
8 $(211)_B$ $71.75$ $71.72 a = 3.225$ 9 $(20\overline{2}0)_{\alpha}^{"}$ $74.64$ $74.61$ 10 $(11\overline{2}2)_{\alpha}$ $76.61$ $76.65$ 10 $(11\overline{2}2)_{\alpha}^{"}$ $76.61$ $76.58$ $(221)_{\alpha}^{"}$ $76.61$ $76.58$ $(21)_{\alpha}^{"}$ $77.69$ $77.85$ 11 $(20\overline{2}1)_{\alpha}$ $77.69$ $77.85$ 12 $(0004)_{\alpha}^{"}$ $82.45$ $82.60$ 13 $(20\overline{2}2)_{\alpha}$ $87$ $87.28$ 14 $(21\overline{3}1)_{\alpha}$ $111.10$ $109.88$ $a.com$	7	λ λ
9 $(20\overline{2}0)_{\alpha}^{\alpha}$ 74.6474.6110 $(11\overline{2}2)_{\alpha}$ 76.6176.6610 $(11\overline{2}2)_{\alpha}$ 76.6176.58 $(221)_{\alpha}^{\mu}$ 76.6176.3711 $(20\overline{2}1)_{\alpha}$ 77.6977.85 $(040)_{\alpha}^{\mu}$ 77.6976.2912 $(0004)$ 82.4582.6013 $(20\overline{2}2)_{\alpha}$ 8787.28 $(222)_{\alpha}^{\mu}$ 8786.0314 $(21\overline{3}1)_{\alpha}$ 111.10109.88	8	25 λ
10 $(11\overline{2}2)_{\alpha}$ 76.6176.66(221)_{\alpha}"76.6176.58(221)_{\alpha}"76.6176.3711 $(20\overline{2}1)_{\alpha}$ 77.6977.85(040)_{\alpha}"77.6976.37(040)_{\alpha}"77.6976.2912 $(0004)$ 82.4582.6013 $(20\overline{2}2)_{\alpha}$ 8787.28(222)_{\alpha}"8787.19(222)_{\alpha}"8786.0314 $(21\overline{3}1)_{\alpha}$ 111.10109.88	9	λ λ
$(221)_{\alpha}^{"} \qquad 76.61 \qquad 76.37 \\ 76.29$ $11 \qquad (20\overline{2}1)_{\alpha} \qquad 77.69 \qquad 77.85 \\ 77.77 \\ (040)_{\alpha}^{"} \qquad 77.69 \qquad 76.37 \\ 76.29$ $12 \qquad (0004) \qquad 82.45 \qquad 82.60 \\ 82.86$ $13 \qquad (20\overline{2}2)_{\alpha} \qquad 87 \qquad 87.28 \\ 87.19 \\ (222)_{\alpha}^{"} \qquad 87 \qquad 85.95$ $14 \qquad (21\overline{3}1)_{\alpha} \qquad 111.10 \qquad 109.88$	10	λ
11 $(20\overline{2}1)_{\alpha}$ 77.6977.85 $(040)_{\alpha}$ "77.6976.37 $12$ $(0004)$ $82.45$ $82.60$ 13 $(20\overline{2}2)_{\alpha}$ $87$ $87.28$ $(222)_{\alpha}$ " $87$ $87.19$ $(21\overline{3}1)_{\alpha}$ $111.10$ $109.88$		$\lambda_1$ $\lambda_1$
$(040)_{\alpha}^{"} \qquad 77.69 \qquad 76.37 \\ 76.29$ 12 $(0004) \qquad 82.45 \qquad 82.60 \\ 82.86$ 13 $(20\overline{2}2)_{\alpha} \qquad 87 \qquad 87.28 \\ 87.19 \\ (222)_{\alpha}^{"} \qquad 87 \qquad 85.95$ 14 $(21\overline{3}1)_{\alpha} \qquad 111.10 \qquad 109.88$	11	λ
12 $(0004)$ 82.4582.60 82.8613 $(20\overline{2}2)_{\alpha}$ 8787.28 87.19 87 $(222)_{\alpha}$ "8786.03 85.9514 $(21\overline{3}1)_{\alpha}$ 111.10109.88 109.88		$\lambda_1$ $\lambda_1$
13 $(20\overline{2}2)_{\alpha}$ 8787.28 $(222)_{\alpha}$ "8786.03 $(222)_{\alpha}$ "8786.0314 $(21\overline{3}1)_{\alpha}$ 111.10109.88	12	$\lambda_1 \\ \lambda_2$
$(222)_{\alpha}"   87   86.03 \\ 85.95 \\ 14   (21\overline{3}1)_{\alpha}   111.10   109.88 \\ 109.88 \\ 0.007 \\ 0.$	13	λ
14 $(21\overline{3}1)_{\alpha}$ 111.10 109.88		$\lambda_1$ $\lambda_1$
$(222)_{\beta}$ 111.10 111.84 $a_0 = 3.225$	14	$^{\lambda_1}_{25}$

<u>APPENDIX IV:</u> Table A-4. Structural analysis of Ti 6211 annealed at  $800^{\circ}$  for 48 hours in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with CuK<sub>a</sub> radiation.

Peak #	hkl or hkil	20 exp.	20 calc.	CuKa
1	(10 <b>1</b> 0)α	35.38	35.28	λ
2	(0002)a (002)a"	38.58 38.58	38.57 38.85	λ λ
3	(111)α" (110)β	39.52 39.52	39.87 39.52 a <sub>o</sub> =3.225A <sup>0</sup>	λ λ.
4	(10 <b>1</b> 1)a (021)a"	40.48 40.48	40.37 41.40	λ λ
5	(10 <b>1</b> 2)a (112)a"	53.20 53.20	53.25 53.02	λ λ
6	(200)β (no other match)	57.12	57.14 a <sub>o</sub> =3.225A <sup>0</sup>	λ
7	(1120)α	63.05	63.35	λ
8	(10 <b>1</b> 3)a (113)a"	71.0 71.0	71.03 71.03	
9	(211)ß	71.64	71.72 a <sub>o</sub> =3.225A <sup>0</sup>	
10	(2020)a (202)a"	74.64 74.64	74.61 74.68	
10	(11 <b>2</b> 2)a	76.45	76.66	λ
	(221)a"	76.45	76.38 76.37 76.29	$\lambda_1 \\ \lambda \\ \lambda_1$
11	(2021)a	77.77	77.85	λ
	(040)a"	77.77	77.17 77.10	$\lambda_1$ $\lambda_1$ $\lambda_1$
12	(0004)a	82.21	82.60 82.86	λ λ <sub>2</sub>
13	(220)β (no other match)	84.53	85.10 85.01 a <sub>o</sub> =3.225A <sup>0</sup>	$\lambda$ $\lambda_1$
14	(2022)a	86.85	87.28	λ
	(222)a"	86.85	86.03 85.95	$\lambda_1$ $\lambda$ $\lambda_1$
15	(20 <b>2</b> 3)a	102.78	102.89	λ
16	(2130)a (240)a"	106.19 106.19	106.55 106.89	$\lambda_1 \\ \lambda_1$
17	(2131)α (222)β	111.00 111.00	109.88 111.84a <sub>0</sub> =3.225A <sup>0</sup>	$\lambda \lambda_1$

 $\frac{\text{APPENDIX V:}}{\text{Table A-5.}}$ Structural analysis of Ti 6211 annealed at 900<sup>O</sup>C for 48 hours in argon atmosphere and guenched in water at room temperature. Data taken at 22<sup>O</sup>C with CuKa radiation.

Peak #	<u>hkl or hkil</u>	20 expt.	20 calc.	<u>CuKa</u>
1	(10 <b>1</b> 0)∝	35.38	35.28	λ
2	(0002)a (002)a"	38.24 38.24	38.57 38.85	λ λ
3	(111)α" (110)β	39.51 39.51	39.87 39.52 a <sub>o</sub> =3.225	λ λ
4	(1011)a (021)a"	40.14 40.14	40.37 41.40	λ λ
5	(1012)a (112)a"	52.89 52.89	53.25 53.02	λ λ
6	(1120)a	62 <b>.</b> 96 .	63.35	λ
7	(1013)α (113)α" (211)β	71.60 71.60 71.60	71.03 71.03 71.65 a_=3.225	λ λ λ
8	(2020)a (202)a"	74.64 74.64	74.61 74.68	λ λ
9	(1122)a (221)a"	76.46 76.46	76.66 76.58 76.37 76.29	$\lambda$ $\lambda_1$ $\lambda$ $\lambda_1$
10	(0004)a	81.41	82.60 82.86	$\frac{\lambda_1}{\lambda_2}$
11	<b>(</b> 220)β	85.00	85.10 a <sub>0</sub> =3.225	λ
	(004)a"	85.00	83.38 83.39	$\lambda_{1}$ $\lambda_{1}$
12	(2130)a (240)a"	106.25 106.25	106.55 106.89	$\lambda_1 \\ \lambda_1$
13	(2131)α (222)β	111.00 111.00	109.88 111.84 a <sub>0</sub> =3.225	$\lambda_1$ $\lambda_1$

# APPENDIX VI:

Table A-6. Structural analysis of Ti 6211 annealed for 30 minutes at 1070°C in argon atmosphere and quenched in water at room temperature. Data taken at 22°C with  $CuK\alpha$  radiation.

Peak #	hkl or hkil	20 expt.	20 calc.	<u>CuKa</u>
1	(10 <b>1</b> 0)∝	35.31	35.28	λ
2	(0002)a (002)a"	38.44 38.44	38.57 38.85	λ λ
3	(1011)a (021)a"	40.21 40.21	40.37 41.40	λ λ
4	(1012)a (112)a"	53.15 53.15	53.25 53.02	λ λ
5	(1120)a	62.97	63.35	λ
6	(10 <b>1</b> 3)a (113)a"	71.20 71.20	71.03 71.03	λ λ
7	(2020)a (202)a"	74.16 74.16	74.61 74.68	λ λ
8	(11Ž2)a	76.50	76.66 76.58	λ λ1
	(221)a"	76.50	76.37 76.29	$\lambda^{-}_{\lambda_{1}}$
9	(2021)a	77.25	77.85 77.77	λ λ1
	(221)a"	77.25	77.17 77.10	$\lambda^{-}_{\lambda_{1}}$
10	(0004) <sub>a</sub>	81.57	82.60 82.86	$\lambda_1 \\ \lambda_2$
11	(20Ž2)a	86.53	87.28 87.19	λ λ1
	(222)a"	86.53	86.03 85.95	$\lambda$ $\lambda_1$
12	(10 <b>1</b> 4)α	92.24	93.10 93.40	$\lambda_1 \\ \lambda_2$
13	(2023)a	102.25	102.89	λ
14	(2131)a	110.00	109.88	λ1

Peak #	<u>hkl or hkil</u>	20 expt.	<u>2θ calc.</u>	<u>Cuka</u>
1	(10 <b>1</b> 0)a	35.30	35.28	λ
2	(0002)a (002)a"	38.55 38.55	38.57 38.85	λ λ
3	(111)α" (110)β	39.60 39.60	39.87 39.71	λ λ
4	(10 <b>1</b> 1)a (021)a"	40.35 40.35	40.37 41.40	λ λ
5	(1012)a (112)a"	53.15 53.15	53.25 53.02	λ λ
6	(1120)a	63.30	63.35	λ
7	(10 <b>1</b> 3)α (113)α" (211)β	71.70 71.70 71.70	71.03 71.03 72.00	λ λ λ
8	(2020)a (202)a"	74.60 74.60	74.61	λ λ
9	(1122)a	76.52	76.66	λ
	(221)a"	76.52	76.38 76.29	$\lambda_1$ $\lambda_1$
10	(2021)a	77.60	77.85	λ
	(040)a"	77.60	77.17 77.10	$\lambda_1 \\ \lambda \\ \lambda_1$
11	(0004) <sub>a</sub>	82.20	82.60 82.86	$\lambda \\ \lambda_1$
12	(2023)a	102.70	102.89	λ1
13	(2130)a (240)a"	106.02 106.02	106.55 106.89	$\lambda_1 \\ \lambda_1$
14	(2131)α (222)β	111.91 111.91	109.88 112.46	$\lambda_1 \\ \lambda_1$
15	(1124)a	114.50	115.06	λ

## APPENDIX VIII:

# Accurate lattice parameter calculation for cubic structures with correction in sample displacement (100).

Applying the case of the Debye-Schemer Camera to the Diffractomer System

 $\frac{\Delta d}{d} = \frac{\Delta a}{a} = K \cos^2 \theta \dots (A-1)$ where K  $\cos^2 \theta$  is the extrapolation function.  $\underline{\Delta d}$  = fractional error in the interplanar spacing, d.  $\Delta a$  = fractional error in the lattice parameter, a. = Bragg angle θ  $K = 2\delta/R$  $\delta$  = sample displacement R = the correct distance for the peak to be if  $\delta = 0$ . Cohen (100) applied the least square method directly to the observed  $\sin^2 \Theta$  values. Squaring the Bragg Law and taking logarithms of each side and differentiating the result is  $\frac{\Delta \operatorname{Sin}^{2} \theta}{\operatorname{Sin}^{2} \theta} = \frac{-2\Delta d}{d} \qquad (A-3)$ Putting this equation into equation A-1 it is seen that the error in  $Sin^2\theta$ varies with  $\theta$ :  $\Delta \sin^2 \theta = -2K \sin^2 \theta \cos^2 \theta = D \sin^2 2 \theta$ where D is a new constant. This equation is valid if  $\cos^2\theta$  is the correct extrapolation

function.

Exptal values of  $\sin^2\theta$ ;  $\alpha$ , and  $\delta$  are now substituted into (A-5) for each diffraction line. This gives n equations in the unknown constantsCC and A and these can be solved for C and A by least square method.

In the present experiment the extrapolation function is K  $\cos^2\theta/\sin\theta$  as shown in the Figure A-1.





$$\frac{\sin \Delta 2\theta}{\delta/\sin \theta} = \frac{\sin (180-2\theta)}{R} \qquad (A-7)$$

$$\Delta 2\theta = \frac{-2\delta \cos \theta}{R}$$

from Bragg's Law

$$\frac{\Delta d}{d} = \frac{1}{\tan \theta} \cdot \frac{\Delta 2\theta}{\sin \theta} = \frac{\cos \theta}{\sin \theta} \cdot \frac{2 \cdot \delta \cos \theta}{R} = \frac{K \cdot \cos^2 \theta}{\sin \theta} = \frac{\Delta a}{a} \cdot \cdot \cdot \cdot \cdot \cdot \cdot (A-8)$$
thus the extrapolation function that is valid is  $\frac{K \cdot \cos^2 \theta}{\sin \theta}$ 

for a cubic sample the folllowing can be written based on Cohen's procedure. By squaring the Bragg's Law and taking the logarithms of each side this is obtained

In 
$$\sin^2 \theta = \ln \frac{\lambda^2}{4} - 2 \ln d \dots$$
 (A-9)

On differentiating

$$\frac{\Delta \sin^2 \theta}{\sin^2 \theta} = -\frac{2 \Delta d}{d}$$

Putting in (27)

$$\Delta \sin^2 \theta = -2 \frac{K \cos^2 \theta}{\sin \theta} \quad \text{Sin}^2 \theta = -2 K \cos^2 \theta \sin \theta$$
  
Sin<sup>2</sup> $\theta$  (true) =  $\lambda^2/4a_0^2 (h^2 + k^2 + 1^2) \quad \dots \quad \dots \quad \dots \quad (A-10)$ 

where  $a_0$  is the true lattice parameter.

But

$$Sin^{2} \theta(obs) = Sin^{2}\theta (true) = \Delta Sin^{2}\theta .$$
  

$$Sin^{2}\theta - \lambda^{2}/4a_{0}^{2} (h^{2} + k^{2} + 1^{2}) = -2K \cos^{2}\theta Sin\theta = -2K Sin2\thetaCos\theta =$$
  

$$D Sin^{2} Cos\theta .$$
  

$$Sin^{2}\theta = \lambda^{2}/4a_{0}^{2} (h^{2} + k^{2} + 1^{2}) + D Cos \theta Sin2 \theta.$$
  

$$Sin^{2}\theta = C\alpha + A\delta$$

where

 $\alpha = (h^{2} + k^{2} + 1^{2})$   $c = \lambda^{2}/4a_{0}^{2}$  A = D/10  $\delta = 10 \cos\theta \sin 2\theta$ The linear equations are of the form

 $\Sigma \alpha \sin^2 \theta = C \Sigma \alpha^2 + A \Sigma \alpha \delta$  $\Sigma \alpha \sin^2 \theta = C \Sigma \alpha \delta + A \Sigma \alpha \delta$ 

APPENDIX IX:

# Accurate lattice parameter calculation of the hexagonal close packed phase (101).

Using the formula developed by Straumanis (101) Klug and Alexander (102), thus if  $h_1$ ,  $k_1$ ,  $l_1$ ,  $\theta_1$  refer to one reflection and  $h_2$ ,  $k_2$ ,  $l_2$ ,  $\theta_2$  to the other, the quadratic forms of the Bragg equations for each reflection may be combined for the hexagonal crystals to obtain the following expressions

$$a = \lambda \frac{1^{2} (h_{2}^{2} + h_{2}k_{2} + k_{2}^{2}) - 1^{2} (h_{1}^{2} + h_{1}k_{1} + k_{1}^{2})^{1/2}}{3(1^{2}_{1} \sin^{2}_{\theta_{2}} - 1^{2}_{2} \sin^{2}_{\theta_{1}})} \qquad (A-11)$$
  
$$c = \frac{\lambda a 1}{2} \left[ \frac{3}{3a^{2} \sin^{2}_{\theta_{2}} - \lambda^{2} (h^{2} + hk + k^{2})} \right]^{1/2} \dots (A-12)$$

APPENDIX X:

## <u>Calculation of volume fractions of $\alpha', \beta$ using the direct comparison</u> <u>method</u>:

This method (102) is used because the retained beta content is very small.

The expression for the intensity diffracted by a single phase powder specimen in a diffractometer is

$$I = \frac{I_0 e^4}{m^2 c^4} \frac{\lambda^3 A}{32\pi\gamma} \frac{1}{v^2} / F/^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \frac{e^{-2M}}{2\mu} \cdots \cdots \cdots \cdots (A-13)$$

I = integrated intensity per unit length of diffraction line

 $I_{o}$  = intensity of incident beam

e,m = charge and mass of the electron

r = radius of diffractometer circle

A = cross-sectional area of incident beam

- v = volume of unit cell
- F = structure factor
- p = multiplicity
- $\theta$  = Bragg angle

 $e^{-2}m$  = temperature factor

 $\mu$  = linear absorption coefficient

The diffracted intensity = I =  $\frac{K_2 K}{2\mu}$  where  $K_2$  is a constant, independent of the kind and amount of the diffracting substance, and R depends on  $\theta$ ,

hkl and the kind of substance. Assuming the alpha prime and beta are the only phases present from the as-quenched sample

$$I_{\alpha'} = \frac{K_2 R_{\alpha'} C_{\alpha'}}{2\mu_m}$$
$$I_{\beta} = \frac{K_2 R_{\beta} C_{\beta}}{2\mu_m}$$

Dividing

$$\frac{I_{\alpha'}}{I_{\beta}} = \frac{R_{\alpha'} C_{\alpha'}}{R_{\beta} C_{\beta}} \qquad (A-15)$$

$$\frac{I_{\alpha'}}{I_{\beta}} \text{ is obtained from the diffraction experiment, } \frac{R_{\alpha'}}{R_{\beta}} \text{ is calculated,}$$
hence  $C_{\alpha'}$  is determined. Combining this value of  $C_{\alpha'}$  with the fact
$$\frac{C_{\alpha'}}{C_{\beta}}$$
that  $C_{\alpha'} + C_{\beta} = 1$ , volume fractions of  $\alpha'$  and  $\beta$  are determined.

APPENDIX XI: Extinction rule for orthorhombic structure



Atom positions after (31)(0,0,0),(1/2,1/2,0), (1/2,1/6, 1/2), (0,2/3,1/2).

Figure A-2. Orthorhombic cell.  
Generally structure factor 
$$F = \prod_{1}^{n} f_n e^{2\pi i (hu_n + kv_n + Lw_n)}$$
 thus the  
structure factor of the orthorhombic cell =  $F_0 = fe^{2\pi i (0)} + fe^{2\pi i (h/2 + k/2)} + fe^{2\pi i (h/2 + k/6 + L/2)} + fe^{2\pi i (2/3k + 1/2L)} = [1 + e^{\pi i (h+k)} + e^{\pi i (h + k/3 + L)} + e^{\pi i (4/3k + L)}] \cdot \dots \cdot (A-16)$   
I. If h + k is odd (in which case h:even, k:odd or h:odd, k even)  
then 1 +  $e^{\pi i (h + k/3 + L)} + e^{\pi i (k + k/3 + L)}$   
=  $fe^{\pi i (h + k/3 + L)} + e^{\pi i (k + k/3 + L)}$   
=  $fe^{\pi i (h + k/3 + L)} + e^{\pi i (k + k/3 + L)}$   
=  $fe^{\pi i (L + k/3)} [e^{\pi i h} + e^{\pi i k}] = 0$   
If h + k is odd  $(F/^2 = 0$ 

II. If h + k is even (in which case h even, k even or h odd, k odd)
from equation A-16
$$F = f (2 + e^{\pi i (h + k/3 + L)} + e^{\pi i (k + k/3 + L)} = f[2 + e^{(k/3 + L)}(e^{\pi i h} + e^{\pi i k})] \dots (A-17)
from (II)
II.a. If h: even, k: even then  $e^{\pi i h} + e^{\pi i k} = 2$ 

$$F = f[2 + e^{(k/3 + L)}(2)] \text{ from equation A-17}$$

$$F = 2f (1 + e^{\pi i (k/3 + L)}).$$
Let  $g_1 = k/3 + L$ .
then  $F = 2f(1 + e^{\pi i g_1})$  (1 +  $e^{-\pi i g_1})$ 

$$= 4f^2(1 + e^{\pi i g_1} + e^{-\pi i g_1})$$

$$= 4f^2(2 + 2 \cos(\pi g_1))$$

$$= 8f^2(1 + \cos^2(\pi f_2)) \dots (A-18)$$
II.a.1. If K = 3 m, then  $g_1 = 3m/3 + L = m + L$ .
If  $m + L$  is odd, that is  $g_1$  is odd and  $L (odd)$ , from
equation A-18
then  $/F/^2 = 0$ .
II.a.2. If K = 3m, then  $g_1 = \frac{3m-1}{3} + L$ 

$$g_1 = m + L - 1/3.$$
II.a.3. If k = 3m - 1 then  $g_1 = \frac{3m-1}{3} + L$ 

$$g_1 = m + L - 1/3.$$
If  $m + L$  is even, L (odd) then from equation A-18
$$/F/^2 = 16 f^2 \cos^2(\pi/2 \cdot (m + L - 1/3)]$$

$$= 16 f^2 \cos^2((m/2 \cdot (m + L - 1/3))]$$

$$= 16 f^2 \cos^2((m/2 \cdot (m + L - 1/3))]$$$$

Summary for condition II.a: h:even, k:even:

if k = 3m and L is odd 
$$/F/^2 = 0$$
  
if k = 3m and L is even  $/F/^2 = 16f^2$   
if k = 3m ± 1 and L is odd  $/F/^2 = 12f^2$   
if k = 3m ± 1 and L is even  $/F/^2 = 4f^2$ .  
Condition II.b:  
If h is odd, k is odd  
then equation A-17 becomes  
 $F = f[2 + e^{(k/3 + L)}(-2)] = 2f(1 - e^{\pi i}(k/3 + L))$   
Let  $g_1 = k/3 + L$   
 $F = 2f(1 - e^{\pi i}g_1)$   
 $/F/^2 = 4f^2(1 - e^{\pi i}g_1)(1 - e^{-\pi i}g_1)$   
 $= 4f^2(2 - 2\cos(\pi g_1))$   
 $= 8f^2(1 - \cos(\pi g_1))$   
 $= 8f^2 \cdot 2 \sin^2(\pi/2 \cdot g_1) = 16f^2 \sin^2(\pi/2 \cdot g_1) \dots (A-19)$   
II.b.1. If k = 3m, then  $g_1 = m + L$   
If m + L is odd (and L even)  
equation A-19 becomes  
 $/F/^2 = 16f^2 \sin^2(\pi/2 \cdot m + L)$   
 $= 16f^2 (\frac{t}{1})^2 = \frac{16f^2}{1}$ .  
II.b.2. If k = 3m then  $g_1 = m + L$   
If m + L is even (and L odd),  
equation A-19 becomes  
 $/F/^2 = 16f^2 \sin^2(\pi/2 \cdot m + 1) = 0$ 

.
II.b.3. If k = 3m - 1, then 
$$g_1 = \frac{3m - 1}{3} + L$$
  
 $g_1 = m + L - 1/3$   
 $/F/^2 = 16f^2 \sin^2(\pi/2 \cdot (m + L) - \pi/6) \cdot \text{ from equation } A-19$   
if m + L is odd (L odd)  
 $/F/^2 = 16f^2 (\sin^{(m + L)}\pi/2 \cos^{(m + L)}) = \pi/6)^2$   
 $= 16f^2 (\frac{1}{2}\sqrt{3})^2 = 12f^2$   
II.b.4. If k = 3m - 1, then  $g = \frac{3m - 1}{3} + L$   
 $g_1 = m + L - \frac{1}{3}$   
from equation  $A-19$   
 $/F/^2 = 16f^2 \sin^2(\pi/2(m + L) - \pi/6)$   
If m + L is even, (L even)  
 $/F/^2 = 16f^2 [-\cos(m + L) \pi/2 \sin \pi/6]^2$   
 $= 16f^2(\frac{1}{2})^2 = 4f^2$   
II.b.5. If k = 3m + 1 then  $g_1 = m + L + 1/3$   
from equation  $A-19$   
 $/F/^2 = 16f^2 \sin^2(\pi/2(m + L) + \pi/6)$   
If m + L is even (L even)  
 $/F/^2 = 16f^2 [\cos(\pi/2(m + L)] \sin \pi/6]^2$   
 $= 16f^2 (\frac{1}{2})^2 = 4f^2$  same as II.b.4.  
II.b.6. If k = 3m + 1 then  $g_1 = m + L + \frac{1}{3}$   
from equation  $A-19$   
 $/F/^2 = 16f^2 \sin^2[\pi/2(m + L) + \pi/6]$   
if m + L is odd (and L odd)  
then  $/F/^2 = 16f^2 (\sin \pi/2(m + L) \cos \pi/6)^2$   
 $= 16f^2 (\frac{1}{2}\sqrt{3})^2 = 12f^2$  same as II.b.3.

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Summary for condition II-b (h:odd, k:odd): if k = 3m and L is even  $/F/^2 = 16f^2$ if k = 3m and L is odd  $/F/^2 = 0$ if K = 3m ± 1 and L is even  $/F/^2 = 4f^2$ if k = 3m ± 1 and L is odd  $/F/2 = 12f^2$ 

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Based on the above derivations the diffracting planes in orthorhombic structure with atom positions at (0,0,0); (1/2, 1/6, 1/2) and (0, 2/3, 1/2). are (110); (020); (002); (111); (021); (112); (022); (200); (130); (023); (113); (220); (202); (221); (040); (004); (222); (114); (024); (223); (310); (311); (240).



Fig. A-3. Atomic scattering factor of titanium versus  $\text{sin}\theta/\lambda.$