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A STUDY OF PHASE EQUILIBRIA IN Ti-6WT%A1-2WT%Nb-1WT%Ta-0.8WT%Mo ALLOY

By

Subhasish Sircar

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

A STUDY OF PHASE EQUILIBRIA IN Ti-6WT%A1-2WT%Nb-1WT%Ta-0.8WT%Mo ALLOY

By

Subhasish Sircar

Microstructure, morphology and crystal structure of various isothermal and athermal phases in Ti 6211 alloy produced by isothermal aging in the temperature range of 1050°C to 600°C and subsequent quenching, have been investigated. It is suggested that whether the a" (orthorhombic) or the a' (hcp) martensite forms, depends on the lattice parameter of the β -phase at the martensite start temperature. This lattice parameter is determined by the solute content of the β -phase and it determines the Bain Strain associated with the martensitic transformation. The β -lattice parameter is found to be decreasing with decreasing isothermal holding temperature and thus the Bain strain decreases with lower heat treatment temperatures. The lattice parameters of the a" martensite at room temperature, corresponding to the maximum volume percent of this phase, are determined to be: a=3.04Å, b=4.94Å, c=4.64Å and the lattice parameter of the β -phase was determined to be: a $_{\beta}$ =3.23Å. DEDICATED TO MY MOTHER

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CHAPTER 1

INTRODUCTION

Ti-6A1-2Nb-1Ta-0.8Mo (Ti 6211) alloy was developed for structural applications in marine environments. Structural materials for marine applications are required to exhibit good resistance to corrosion and stress corrosion cracking, high fracture toughness, good specific strength and good weldability of the material. the microstructure of a near α or $\alpha + \beta$ alloy such as the Ti 6211 has a great influence on various mechanical properties such as strength, ductility and fracture toughness. Therefore it is important to understand the nature and origin of the microstructural features of this alloy system. Once this is accomplished, the relation between microstructure, composition and thermal history of this class of alloy should be easier to understand.

 $(\alpha + \beta)$ alloys generally (1) have good low cycle fatigue properties because of fine grained mixture of $(\alpha + \beta)$ structures with relatively high proportions of primary α . Fracture toughness can be improved by raising the solution temperature to give a microstructure with coarser Widmanstatten α transformed from β . Ductility can be retained at the same time having dispersed fine martensitic phases. The β - 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 specially in the transverse directions of rolling (1). Hence β - Ti alloys have restricted use especially in forgings or sheet

rollings (1).

A host of microstructural features can be produced in Ti-6211 by varying hot working conditions, heat treatment and variations in quenching or cooling rates. Apart from the microstructural variations produced by 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 diffusional decomposition, there are several diffusionless and martensitic phases. Depending on the heat treatment in the $\alpha + \beta$ field, meta-stable β -phase can be retained (2) in Ti 6211 alloy. A possibility exists that such a meta-stable 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 values of yeild strength, low values of elastic modulus and high internal friction to the stress induced martensitic transformations of the meta-stable β - 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 of transformation, formation and stability of these phases and solute partitioning at various times and temperatures has been done.

A unified investigation of the above mentioned aspects of the asquenched and aged Ti 6211 is accomplished by the present study. In addition accurate lattice parameters of these phases are calculated and the lattice correspondence and crystallography proposed by Mukherjee and Kato (4) are described for possible application to Ti 6211.

CHAPTER 2

REVIEW OF PREVIOUS STUDIES

There is much scattered information concerning phase transformations in titanium alloys in the literature. In this review an attempt is made to bring these pieces of information under the same heading in a systematic manner.

2.1 Titanium Alloys

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 (5).

(i) The Alpha System

Figure 1 represents a typical binary constitution diagram of alloying elements that stabilize the alpha phase. 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 the alpha than in the beta phase. 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 beta-isomorphous, Figure 2. Those beta-stabilizers that are not miscible with the beta phase in an eutectoid reaction into beta eutectoid,



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

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



Fig. 2. Partial Phase Diagram of the Beta Isomorphous System.

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



Alloy Content

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

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

Figure 3. The beta eutectoid elements which decompose the beta phase into alpha and intermetallic phase are Mn, Fe, Cr, Co, Ni and Si.

Unlike the alpha and beta 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 as dispersoids. Constitutional diagrams of Ti-Al, Ti-Ta, Ti-Nb and Ti-Mo systems, which are relevant to Ti 6211 are shown in Figures 4 to 7 (5,6,7).

2.2 Phases and Phase Transformations in Titanium Alloys

Phase transformations and product phases in titanium alloys can be classified into eight groups after Murakami (8) :

- Decomposition of beta phase during quenching producing alpha prime, alpha double prime, face centered orthorhombic martensite, athermal omega and retained beta.
- 2. Isothermal transformation of metastable beta phase producing isothermal omega, alpha double prime, beta prime, alpha, α_2, β_2 .
- 3. Decomposition of retained beta phase producing isothermal omega, beta prime, Widmanstatten alpha, raft alpha, α_2 , β_2 stress-induced martensite, thermoelastic martensite and isothermal martensite.
- Decomposition of martensite producing alpha, a compound and beta.
- Alpha phase formation through omega and beta prime intermediate phase formation.
- Eutectoid decomposition, pearlitic constituent or massive product.
- 7. Precipitation from alpha-solid solution producing a compound



Figure 4. Constitutional diagram of titanium-aluminum system.



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

.



Figure 6. Constitutional diagram of titaniumtantalum system.



Figure 7. Ti-Ta Phase Diagram

and α_2 phase.

8. Formation of alpha/beta interphase during slow cooling.

A brief explanation of the above phases are given below :

- Beta phase: A high temperature allotrope of titanium with a body centered cubic crystal structure (BCC).
- 2. Alpha : The low temperature allotrope of titanium with hexagonal close packed crystal structure (HCP).
- 3. Alpha prime: A hexagonal martensite. It is a supersaturated, non-equilibrium alpha phase formed by a diffusionless transforof the beta phase.
- 4. 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 phase that forms either by quenching from beta phase field below the omega start temperature or isothermal aging of beta-titanium alloys.
- Beta prime: Decomposition product of metastable beta. It is a solute lean BCC zone.
- 7. β_2 : Ordered BCC phase formed by decomposition of retained beta. Its formula is Ti₂ MoAl in Ti-Mo-Al alloys.
- 8. a2: Ordered phase based on Ti Al in Ti-Al alloy system.
- 9. Interface phase: A beta decomposition product that forms along alpha/beta interfaces of Widmanstatten structures.

2.3 Morphology of Equilibrium Phases in Titanium Alloys

The nucleation and growth of alpha phase after cooling from the beta region results 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, plates often form in colonies or stacks. The formation of the colonies and the basketweave microstructures depend on the cooling rate from beta or $(\alpha + \beta)$ regions and the alloy chemistry. At times alpha nucleates on the prior-beta grain boundary forming grain boundary alpha. Such alpha grows along the boundary and frequently leads to continuous grain boundary alpha. Another morphology of alpha reported by F. S. Lin et al (9) is known as 'blocky alpha' or 'sphagetti alpha', which is formed when there is not many sites for nucleation of alpha. Another morphology of alpha which results from hot working and thermomechanical processing is equilibrium equiaxed alpha.

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. Another very common morphology is the acicular martensite morphology. 'Butterfly' martensite is another morphology of the titanium alloy martensites. It has been observed in Ti 6211 alloy. This morphology results from the formation of plates along two adjacent variants. It is beleived that this morphology can give rise to self accomodation of transformation strain energy.

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 (10, 11) and acicular martensite (11,12,13).

The massive martensite was found to consist of colonies which were resolvable optically (11). 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 (11).

With increasing solute (decreasing Ms temperature) the massive martensite colony size was found to decrease (14) and at a solute concentration which was shown to vary between alloy systems, the colonies totally degenerated to individual plates (13), each being a different variant of the orientation relation.

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 double prime (15,16,17). Habit plane determination on the acicular martensite have been performed and these martensites have, for most part, the {334} beta habit plane (13,17, 18) which had been predicted by Bowles and Mackenzie crystallographic theory of martensite. Several workers have also predicted a {334} beta (11, 17) habit plane.

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

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 over a wide range of composition (19). Alpha double prime was recently observed in the commercial α + β alloy Ti-6A1-2W-4Zr-6Mo and its

occurence in this alloy was shown to be accompanied by a reduction in tensile ductility (20). The lattice parameters of orthorhombic martensite were strongly composition dependent (14, 21). Davis et al (22) recently proposed that the transition in martensite crystallography from hexagonal to orthorhombic occured with increasing solute content and decreasing Ms, (as shown in Table 1) and that atleast one alpha double prime free energy. They proposed a form of free energy/composition relationship 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 the Ms of the beta phase.

Before going into the crystallographic aspects of titanium alloy martensites, it would be appropriate to refer to the work of Williams (23), where he proposes a schematic phase diagram of Ti 6211 alloy, figure 8. In this figure he shows the alpha, beta phase field and also qualitatively predicts the Ms hexagonal and Ms orthorhombic lines in this alloy system. This figure will be discussed in detail in the results and discussion section of this thesis.

2.4.3 Crystallography of α ' and α " Martensites

The Burgers' mechanism for the beta (BCC) to alpha prime (HCP) transformation (24) in titanium alloys is still tenable. Also the formation of alpha double prime martensite and alpha prime martensite can be explained in terms of the beta stabilizing element composition and simple atomic shuffling.(figure 9).

Oka and Taniguichi (25) 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 (26) confirmed that

7	εl	^е 2	е ₃	martensite
ure Ti -	-10.1	10.1	06.0	5
1-2% Mo	-10.2	10.0	0.91	້ອ
1-4% Mo	-10.2	10.0	0.91	້ອ
1-6% Mo	-9.5	8.9	0.65	= 8
1-8% Mo	-8.5	7.8	0.37	= 8

Table 1:	Effect	of M	uo o	the	type	of	martensite	formation
	in Ti-	do bi	nary	allc	ys			



Figure 8: The schematic phase diagram of Ti 6211



.



with increasing beta stabilizing agent the crystal structure of titanium martensites changes from hexagonal to orthorhombic. Duerig et al (27) and Sasano et al tried to explain the transformation of beta to alpha prime or alpha double prime martensite by simply atomic movements.

In addition to the alpha prime and alpha double prime martensite face centered orthorhombic martensite was obtained in Ti-12V alloy bulk crystal (28). It has been pointed out that all titanium martensites $(\alpha', \alpha'', f.c.o)$ can be generated from a face centered tetragonal equivalent of the four unit cells of the BCC beta phase (Figure 10).

Mukherjee and Kato (4) unified these physical interpretations of transformations of beta to alpha prime or alpha double prime and proposed that for the alpha prime, the Bain strain is brought about by Burgers' mechanism where the operation of the $\{112\}<111>_{\beta}$ shear systems followed by a small volume increase results in the $(0001)_{\alpha}$, plane from the $(011)_{\beta}$ plane. In addition to the above Bain strain a $a_{\beta}[0\overline{11}]/6$ shuffling on every other $(011)_{\beta}$ plane is necessary to create the hexagonal structure.

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>_B shears, the (O11)_B plane does not completely change to the hexagonal close packed plane but stops midway between the (O11)_B and (O001)_a, leaving the angles θ_1 and θ_2 (Figure 11) slightly different from 120 degrees. Thus the alpha double prime 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 (28). From the Bain strains calculated in Ti-12.6V by Mukherjee and Kato (4) for the f.c.o. martensite unlike alpha prime and alpha double prime cannot be considered a "distorted"



Figure 10: Lattice correspondence of martensites showing the four unit cells of the BCC crystal and its face centered tetragonal equivalent.



Figure 11: Crystal structure change from BCC to (a) HCP and (b) orthorhombic

alpha prime martensite. Mukherjee and Kato (4) have also shown by strain energy minimisation criteria and by Bain strain calculation that there exists a critical Bain strain at which a transition from alpha prime to alpha double prime martensite is favorable. This means that the transformation of beta to alpha double prime is more favourable than beta to alpha prime for certain critical solute concentration of the beta phase. In Ti 6211 alloy a mixture of the two types of the martensites (alpha prime and alpha double prime) is also a possibility in the light of the phase equilibria described in Figure 8. Of the various alloying elements in Ti 6211, Mo produces a contraction in the beta lattice parameter and thus tends to favour the alpha double prime formation.

2.5 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-6A1-4V. The interface phase has a somewhat variable morphology (29). 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 (30,31). 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 (29) suggested that it is 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 of these have some difficulties associated with it. For example, Rhodes and Williams (29) 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 (32) 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 the case as shown in (30). Secondly, if the interface phase is simply localised mechanical twinning, then each twin should have accomodation dislocations in the matrix ahead of its terminus; generally this is not the case. Finally, Rhodes and Williams reported a monolithic face centered 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 (33) found that in Ti 685 the alpha/beta interface phase was of two forms, the monolithic (ML) and the striated (SL) and was dependent on homogenisation temperature in the β or $\alpha + \beta$ phase field and the cooling rate. The layers have FCC crystallographic structure and in twin relationship with the <111> ML twin axis. The formation of the in 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.

Banerjee and Arunachalam (34) in their study of two titanium alloys IMI 685 and BT9 maintained that the FCC interface phase does not form as part of the transformation sequence beta to FCC to alpha, it rather had precipitated on the alpha side of the alpha/beta interface at a fairly late stage of the beta to alpha transformation. They concluded that beta is retained whenever the beta to alpha transformation occurs by

nucleation and growth and the interface phase is observed all alpha lath/ retained beta interfaces, but not when the beta to alpha transformation is martensitic. However, Banerjee and Williams (35) in a recent paper suggested that the face centered cubic and hexagonal structure which was reported earlier as the interface phase structure are in fact artifacts produced by the electrolytic technique used in thin foil preparation.

2.6 α_2 Phase

The alpha phase which contains 10 at% Al is supersaturated and can decompose during aging at 500°C. The decomposition of Ti-Al alloy containing 10 at% Al has been observed by many workers (36,37) and there is an ordered phase based on Ti₃Al. This product is usually designated the α_2 phase and has a DO₁₉ structure. Only relatively recently it was shown that the α_2 phase formed as uniformly distributed, coherent precipitates (37). Further, the exact position and the extent of the $\alpha + \alpha_2$ phase field is still subject to some question (38,39). The morphology of coherent α_2 during early stages of formation is equiaxed whereas at later stages (larger sizes) it is ellipsoidal 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] and0.83% perpendicular to [0001]. The α_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 α_2 in Ti-Al alloys is the amount of oxygen present as an impurity. Paris and Williams recently investigated the role of oxygen in α_2 formation (40) and found that a 2000 wt. ppm. increase in oxygen content in a Ti-7.3 wt% Al led to an increase of 100°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 α -Ti lattice which increases the misfit of α_2 , atleast when the unconstrained lattice parameters of the 'pure' α and α_2 phases are considered. This would be expected to suppress the coherent solvus rather than raise it. Gehlen (41) has suggested that the structure of the α_2 phase is distorted and has used X-ray diffraction measurements and intensity calculations to support this. Assuming that the distortion described by Gehlen really exists some of the octahedral holes in the α_2 lattice will be expanded. This tends to increase solubility of oxygen in the α_2 phase. On the basis, Paris and Williams (40) suggested that oxygen partitions to the α_2 phase and stabilizes it to higher temperatures.

2.7 Beta Phase

In alloys which contains between 7 and 25at% Al the addition of sufficient quantities of beta stabilising elements still permits retention of the BCC allotropic form during quenching. These 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 (42) designated β_2 (43). The beta 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 100 volume percent β_2 during quenching (44,45,46). This beta phase contains fairly large antiphase domains; this suggests that the order disorder temperature for formation of β_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 to 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 the A and B sites in the AB superlattice. Even if it is assumed that Ti occupies the A sites and all other solutes occupy the B sites, there typically are insufficient B atoms to achieve stoichiometry. Therefore the B2 lattice must be stable over a wide composition range.

2.8 The Phenomenological Crystallographic Theory of Martensitic Transformation

The phenomenological crystallographic theory of displacive martensitic transformations was developed simultaneously by Wechsler, Liberman and Read (47) and Bowles and Mackenzie (48). In 1924 Bain (49) 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 expansion of about 12% in the plane perpendicular thereto, Figure 12. This Bain model and many other theories summarized by Cohen (50) were not able to account for all of the important crystallographic features of the martensitic transformation in a self-consistent manner, that is, if the crystal structure change was correctly described, the habit plane and/or orientation relationship usually was not.



Figure 12. 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 13. Schematic representation of inhomogeneous lattice-invariant shear by (a) internal twinning and (b) internal slip within martensite plates after (81).



Figure 14. Sphere-ellipsoid representation of homogeneous deformation in which matching planes of no distortion exist (cross-hatched) after (81).

The W-L-R theory 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 deformetion.

2. A shear deformation which maintains the lattice symmetry (does not change the crystal structure)and, in combination with the Bain distortion produces an undistirted 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 12, 13, 14.

No attempt was made 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. On the other hand Bowles and Mackenzie (48) theory almost identical but mathematically somewhat different to the W-L-R theory has adjustable parameters in the form of a uniform dilatation in the interface (habit plane). The surface dislocation approach of Bullough and Bilby (51) is most closely related to the matching method of Frank (52) and Bilby and Frank (53). For excellent summaries and critical reviews of the theoretical and experimental work on martensitic phase transformations, the reader is reffered to Bilby and Christian (54) and Cohen (50).

CHAPTER 3

EXPERIMENTAL PROCEDURE AND TECHNIQUES

3.1 Heat Treating of Ti 6211

3.1.1 Selection of Test Conditions

Preliminary heat treatment showed that for the sample size used, 30 to 35 minutes was adequate to obtain equilibrium beta phase at the solution treatment temperature of 1050°C. Longer time intervals were chosen to ensure equilibrium at various annealing temperatures below 1050°C. Since titanium is a very reactive material samples were heat treated in vacuum.

3.1.2 Procedures

The as received plate of Ti 6211 was cut into small rectangular blocks, 2cm. by 1cm. by 0.5cm in size, by an abrasive cut off wheel. The samples were then polished in 120 grade abrasive cloth to remove blade marks and flatten the surface. The samples were then encapsulated in a quartz tube under a vacuum of approximately 10^{-5} torr. Proper precautions were taken to avoid heating of the samples during sealing the quartz tube. Purposely some of the samples were heat treated in air to understand the microstructural effects associated with oxygen intake. The samples were initially solution treated at 1050°C and then step quenched at progressively lower temperatures of isothermal holding and then quenched to room temperature. One sample was furnace cooled from 1050°C to study the equilibrium microstructure. The heat treatment

schedule followed is schematically shown in Figure 15.

3.2 Analysis of Heat Treated Samples

3.2.1 Optical Microscopy

For optical microscopy, the heat treated samples were first polished on 240, 320, 400 and 600 emery papers. Final polishing was done on the polishing wheel with microcloth using 0.05 micron alumina. The samples were etched for about 40 seconds (time varying for different heat treatments) in Kroll's etchant which is 95cc H_2O , 3.5cc HNO_3 and 1.5cc HF and then washed in running water and methanol and dried. A Leitz microscope was used for taking micrographs.

3.2.2 X-ray Diffraction

The heat treated samples were cut to proper size to fit the specimen holder. Before taking X-ray diffraction patterns, the sample was polished as above and then lightly etched to remove the distorted layer. A Philips Norelco X-ray diffractometer fitted with a LiF crystal monochromator, was used with CuK_{α} radiation.

3.2.3 Scanning Transmission Electron Microscopy

The sample preparation for observation under the Scanning Transmission Electron Microscope is typical to that of any electron microscopy work. Twin jet polishing was applied before which the specimens were cut by the diamond wafering blade and hand ground on coarse emery paper to the desired thickness. The polishing conditions are given below: (a) Jet Thinning

> Starting thickness 150µm; 3mm. discs. 30 mls. percholoric acid 175 mls. butoxyethanol



Figure 15: Keat treatment schedule

295 mls. ethanol V≃ 120 Volts; 130-140 mA

(b) Final Polishing

6mls. percholoric acid
175 mls. butoxyethanol
295 mls. ethanol
V≃ 12-50 Volts; I≃ 20 mA; T=-45°C to -55°C.

The microscope used was the Vacuum Generators HB 501 Scanning Transmission Electron Microscope. The energy dispersive X-ray mode was utilised to perform chemical analysis of the martensite plates to study the solute partitioning effects in this alloy.

3.2.4 Scanning Electron Microscopy

The specimen preparation was essentially the same as in the case of optical microscopy, the only difference being the fact that in this case the samples were etched a little harder. A Hitachi S-415A Scanning Electron Microscope was used for this study. A polaried camera attachment was used to take micrographs of the sample.

CHAPTER 4

RESULTS AND DISCUSSIONS

In this chapter, at first the microscographs are presented in a systematic manner. Then the X-ray diffraction data are presented to show the relationship of the proposed model by Mukherjee and Kato (4) and the experimental observations. Lastly, the Scanning Electron Microscopy and Scanning Transmission Electron Microscopy data are presented which further corroborates the theoretical model proposed by Mukherjee and Kato (4).

4.1 Microstructures

The first set of micrographs shown in figures 16 to 18 are scanning electron micrographs of samples quenched from 1050°C to room temperature. It shows a predominantly martensitic structure. One martensite plate in Figure 17 is magnified in Figure 18 and it suggests the presence of internal twins in the martensite plates. Figures 19 and 20 are the optical micrographs of samples with the same heat treatment, but in Figure 20 is shown the microstructure of the samples heat treated in air. Oxygen in air being an alpha stabilizers, precipitates out some amount of alpha even when the specimen is quenched from the solution treatment temperature. Refering to Figure 8, it can be suggested that the above microstructure is according to that predicted by the schematic phase diagram. Before proceeding further, let us at first examine the schematic beta-isomorphous diagram shown in Figure 8. In this Figure Ti 6211 alloy

is shown by the vertical line A-B-C-D and the various phase equilibria temperatures for the alloy reported by Williams (23) is also shown. If a sample is held at a temperature such as B, until equilibrium is reached, a certain amount of alpha and a certain amount of beta, according to the tie-line compositions, will separate out. However, at a lower temperature of holding, e.g. at C or D the proportion of alpha phase will increase and the solute concentration of the beta phase will also increase, although the composition of the alpha phase will remain nearly constant. The Ms-hexagonal and the Ms-orthorhombic temperatures, as shown in the Figure 8 by dotted lines, are schematic at the moment since these are not yet verified. We shall again this diagram (Figure 8) subsequently to justify the validity of our experimental findings.

Figures 21 to 23 are optical micrographs of a sample held at 1050°C for half hour and then immediately transferred to 950°C and held for one hour and quenched to room temperature in water. Subsequent references to particular temperature would mean exactly similar heat treatments. Figures 21 and 22 show the precipitation of grain boundary alpha and the basket weave martensitic structure. Figure 23 is the micrograph of the sample with the same heat treatment performed in air and hence the alpha precipitation is higher. Figure 24 shows a sample which has been solution treated at 1050°C for half hour and then immediately transferred to a 900°C furnace and held for one hour and quenched to room temperature. Here the amount of precipitation of grain boundary alpha is primarily the same or slightly more. the basket weave structure as mentioned earlier is also present. Figure 25 is another sample annealed at 900°C (heat treated in air) showing a massive martensitic structure. This kind of martensite has been termed ' butterfly ' martensite (55). Figure 26

is an optical micrograph of a sample heat treated at 850°C in air. This microstructure shows another morphology of alpha known as 'sphagetti' alpha (9). It must be noted that this kind of morphology was not observed for vacuum treated samples. Figure 27 is the microstructure of a sample heat treated at 800°C. Apart from the grain boundary alpha, this scanning electron micrograph also shows a Widmanstatten alpha morphology. Figure 28 is a magnified image of the same structure showing clearly the grain boundary alpha and the Widmanstatten alpha. Figure 29 is a micrograph of a sample heat treated at 700°C. The big increase in the volume of grain boundary alpha in this micrograph is justified as can be seen from Figure 8 where a decrease in the temperature of holding shows an increase in the amount of equilibrium alpha. Figure 30 is an optical micrograph of a sample heat treated at 650°C. It has a microstructure similar to Figure 21, which is for a sample annealed at 950°C. The important feature of this heat treatment is the large increase in the amount of grain boundary alpha due to the same reason as mentioned above. Figures 32 and 33 are scanning electron micrographs of a sample furnace cooled at a cooling rate of approximately 30°C/hour from 1050°C. It shows a distinct alpha/beta network and equilibrium alpha precipitation at the prior beta grain boundary. Figure 33 is a magnified image of the same region which shows in greater detail the morphology of the equilibrium alpha and beta. Figure 34 is the micrograph of a sample furnace cooled in air from 1050°C. This micrograph also shows the alpha/ beta structure and has the same morphology.

From this diversity of microstructure, it is apparent that a careful and systematic study of the crystal structure is necessary in order to understand the various phases present after various heat treatment



Figure 16: SEM micrograph of sample. 1050°C $\frac{1}{2}$ hour, WQ; showing fine martensitic plate structure.



Figure 17: SEM micrograph of sample. $1050^{\circ}C \frac{1}{2}$ hour, WQ; showing the martensite plates at higher magnification. The inset, a martensite plate is shown at higher magnification in figure 18.



Figure 18: SEM micrograph of sample. $1050^{\circ}C\frac{1}{2}$ hour, WQ; showing a martensite plate in detail. Internal twins are visible in this plate.



Figure 19: Optical Micrograph of sample. $1050^{\circ}C^{\frac{1}{2}}$ hour, WQ; showing fine martensitic plate structure.



Figure 20: Optical micrograph of sample heat treated in air. $1050^{\circ}C$ hour, WQ; showing fine martensitic platelets along with fine precipitation of grain boundary alpha.



Figure 21: Optical micrograph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, isothermal holding $950^{\circ}C$ l hour, WQ; showing basketweave martensitic structure along with precipitation of grain boundary alpha.



Figure 22: Optical micrograph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, isothermal holding 950°C l hour, WQ; showing basket weave martensitic structure along with precipitation of alpha along prior beta grain boundary.



Figure 23: Optical micrograph of sample with same heat treatment as in figure 22 in air; showing a higher amount of grain boundary alpha precipitation along with the martensitic structure.



Figure 24: Optical micrograph of sample. $1050^{\circ}C^{\frac{1}{2}}$ hour, isothermal holding 900°C 1 hour, WQ; showing grain boundary alpha and also martensitic structure.



Figure 25: Optical micrograph of sample heat treated in air. $1050^{\circ}C \frac{1}{2}$ hour, isothermal holding 900°C l hour, WQ; showing 'butterfly' martensite and basketweave martensite structure.



Figure 26: Optical micrograph of sample heat treated in air. $1050^{\circ}C_{\frac{1}{2}}$ hour, isothermal holding $850^{\circ}C_{\frac{1}{2}}$ hour, WQ; showing 'sphagetti' alpha precipitation along with basketweave martensitic structure.



Figure 27: SEM microgrsaph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, isothermal holding $800^{\circ}C$ lhour, WQ; showing grain boundary alpha and also Widmanstatten alpha precipitation.



Figure 28: SEM micrograph of sample with same heat treatment as in figure 27; showing the grain boundary alpha and Widmanstatten alpha in greater detail.



Figure 29: Optical micrograph of sample. 1050° C $\frac{1}{2}$ hour, isothermal holding 700°C l hour, WQ; showing basketweave martensitic structure and grain boundary alpha.



Figure 30: Optical micrograph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, isothermal holding $650^{\circ}C$ l hour, WQ; showing large amounts of grain boundary alpha precipitation and basketweave martensitic structure.



Figure 31: Optical micrograph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, isothermal holding $600^{\circ}C$ l hour, WQ; showing basketweave martensitic structure and alpha precipitation along prior beta grain boundary.



Figure 32: SEM micrograph of sample. $1050^{\circ}C$ $\frac{1}{2}$ hour, furnace cooled to room temperature; showing grain boundary alpha and alpha/beta network.



Figure 33: SEM micrograph of sample. $1050^{\circ}C^{\frac{1}{2}}$ hour, furnace cooled to room temperature; showing clearly the alpha/beta network and grain boundary alpha.



Figure 34: Optical micrograph of sample. $1050^\circ C~\frac{1}{2}$ hour, furnace cooled to room temperature; showing grain boundary alpha and the alpha/beta network.

conditions.

4.2 X-ray Diffraction Studies

X-ray diffraction patterns were obtained for all the heat treated samples and the results obtained are tabulated in Tables 2 to10. Two Bragg angle regions have been found to be very important and informative. They are between 20 values of 33° to 43° and 72° to 80°. In these regions, identifiable primary or untransformed beta phase and the orthorhombic martensite phase have been detected. It is for this reason two composite graphs have been drawn to scale in Figures 35 and 36. Figure 35 shows the X-ray diffraction peaks for Bragg angles between 72° and 80° in a composite manner. One noteworthy feature of the result is the (202) $_{
m m}$ peak. This shows a gradual increase in intensity for holding temperatures from 650°C to 900°C followed by a decrease for holding temperatures greater than 900°C. The furnace cooled sample quite obviously does not show any orthorhombic martensite. This result therefore demonstrates that there is a critical range of temperature of heat treatment at which the ratio of alpha double prime to alpha prime is maximum, ie., the formation of alpha double prime martensite is most favoured.

Figure 36 shows a similar type of composite layout of X-ray diffraction profiles between 33° and 43° 20 values. In this figure the important aspect is the $(110)_{\beta}$ peak. We see that there is a shift of the $(110)_{\beta}$ peak to higher angles with decreasing heat treatment temperatures. This means that there is a contraction in the lattice parameter of the retained beta phase with decreasing temperature. From the schematic diagram in figure 8, we notice that at progressively lower temperatures of holding we have an increase in the concentration of the beta solute elements. Since Mo is the only element in Ti 6211 alloy which decreases

Table 2: Experimental 20 (Bragg angles) values for samples heated to 1050°C for $\frac{1}{2}$ hour and water quenched. Data taken at 22°C with CuK $_{\alpha}$ radiation.

Peak #	20 (deg)	(hkil) or (hkl)	Phase Identification
1	35.23	(1010)	α, α'
2	38.50	(0002)	α, α'
3	40.21	(1011)	α, α'
4	53.10	(1012), (112)	α, α',α"
5	63.15	(1120)	α, α'
6	70.77	(10]3), (113)	α, α',α"
7	74.50	(20 <u>2</u> 0) , (2 02)	α, α',α"
8	76.43	(1122), (221)	α, α',α"
9	77.50	(2021)	α, α'
10	82.30	(0004)	α, α'
11	86.97	(2022)	α, α'
12	92.90	(1014), (114)	α, α',α"
13	102.63	(2023), (223)	α, α',α"

Table 3: Experimental 20 (Bragg angles) values for samples heated to 1050°C for $\frac{1}{2}$ hour, step quenched and isothermally held at 950°C for 1 hr., and water quenched. Data taken at 22°C; CuK_{α} radiation

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.40	(10Ī0)	α, α'
2	38.74	(0002)	α, α'
3	40.53	(1011)	α, α'
4	53.33	(1012), (112)	α, α', α"
5	63.37	(1120)	α, α'
6	70.88	(1013), (113)	α, α', α"
7	74.60	(2020), (202)	α, α', α"
8	76.58	(1122), (221)	α, α', α"
9	77.80	(2021)	α, α'
10	82.58	(0004)	α, α'
11	87.22	(2022)	α, α'
12	93.00	(1014), (114)	α, α' α
13	102.80	(20 2 3), (223)	α, α', α"
14	106.50	(2130), (240)	α, α', α"
15	109.65	(2131)	α, α'
16	114.67	(1124)	α, α'

Table 4: Experimental 20 (Bragg angles) values for samples heated to $1050^{\circ}C \frac{1}{2}$ hr., step quenched and isothermally held at 900°C for 1 hr. and water quenched. Data taken at 22°C; CuK_a radiation.

Peak #	20 (deg)	(hkil) or (hkl)	Phase Identification
1	35.30	(1010)	α, α'
2	38.52	(0002)	α, α'
3	40.26	(1011)	α, α'
4	53.20	(1012), (112)	α, α', α"
5	63.18	(1120)	α, α'
6	70.80	(1013), (113)	α, α', α"
7	74.58	(2020), (202)	α, α', α"
8	76.40	(1122), (221)	α, α', α"
9	77.58	(2021)	α, α'
10	82.25	(0004)	α, α'
11	87.15	(2022)	α, α'
12	92.90	(1014), (114)	α, α', α"
13	102.76	(2023), (223)	α, α', α"
14	106.28	(2130), (240)	α, α', α"
15	109.47	(2131)	α, α'
16	114.50	(1124)	α, α'

Table 5: Experimental 20 (Bragg angles) values for samples heated to $1050^{\circ}C \frac{1}{2}$ hr., step quenched and isothermally held at 850°C for 1 hr. and water quenched. Data taken at 22°C; CuK_Q radiation.

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.23	(1010)	α, α'
2	38.40	(0002)	α, α'
3	40.23	(1011)	α, α'
4	53.13	(1012), (112)	α, α', α"
5	63.10	(1120)	α, α'
6	70.72	(1013), (113)	α, α', α"
7	74.50	(2020), (202)	α, α', α"
8	76.40	(1122), (221)	α, α', α"
9	77.60	(2021)	α, α'
10	82.40	(0004)	α, α'
11	87.10	(2022)	α, α'
12	92.80	(1014), (114)	α, α', α"
13	102.69	(2023), (223)	α, α', α"
14	109.70	(2131)	α, α'
15	114.30	(1124)	α, α'

Table 6: Experimental 20 (Bragg angles) values for samples heated to $1050^{\circ}C \frac{1}{2}$ hr., and step quenched and isothermally held at 800°C 1 hr., and water quenched. Data taken at 22°C; CuK α radiation.

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.25	(1010)	α, α'
2	38.45	(0002)	α, α'
3	40.30	(1011)	α, α'
4	53.17	(1012), (112)	α, α', α"
5	63.15	(1120)	α, α'
6	70.72	(1013), (113)	α, α', α"
7	74.47	(2020), (202)	α, α', α"
8	76.42	(1122), (221)	α, α', α"
9	77.60	(2021)	α, α'
10	82.30	(0004)	α, α'
11	87.05	(2022)	α, α'
12	92.73	(1014), (114)	α, α', α"
13	102.47	(2023), (223)	α, α', α"
14	109.67	(2131)	α, α'
15	114.60	(1124)	α, α'

Table 7: Experimental 20 (Bragg angles) values for samples heated to $1050^{\circ}C \frac{1}{2}$ hr., step quenched and held isothermally at 750°C for 1 hr. and water quenched. Data taken at 22°C; CuK_Qradiation.

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.30	(1011)	α, α'
2	38.50	(0002)	α, α'
3	39.30	(110)	β
4	40.30	(1011)	α, α'
5	53.17	(1012), (112)	α, α', α"
6	63.20	(1120)	α, α'
7	70.90	(1013), (112)	α, α', α"
8	76.50	(1122), (221)	α, α', α"
9	77.70	(2021)	α, α'
10	87.06	(2022)	α, α'
11	92.97	(1014), (114)	α, α', α"
12	102.73	(2023), (223)	α, α', α"
13	109.70	(2131)	α, α'

.

Table 8:	Experimental 20 (Bragg angles) values for samples heated to
	1050°C $\frac{1}{2}$ hr., step quenched and held isothermally at 700°C for
	l hr. and water quenched. Data taken at 22°C, CuK $_{\!\alpha}$ radiation.

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.35	(1010)	α, α'
2	38.57	(0002)	α, α'
3	39.37	(110)	β
4	40.37	(1011)	α, α'
5	53.15	(1012), (112)	α, α', α"
6	63.25	(1120)	α, α'
7	70.90	(1013), (113)	α, α', α"
8	76.50	(1122), (221)	α, α', α"
9	77.70	(2021)	α, α'
10	82.50	(0004)	α, α'
11	87.15	(2022)	α, α'
12	92.88	(1014), (114)	α, α', α"
13	102.70	(2023), (223)	α, α', α"
14	109.60	(2131)	α, α'
15	114.57	(1124)	α, α'

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Table 9: Experimental 20 (Bragg angles) values for samples heated to $1050^{\circ}C \frac{1}{2}$ hr., step quenched and held isothermally at 650°C for 1 hr. and water quenched. Data taken at 22°C, CuK_Q radiation.

Peak #	2θ (deg)	(hkil) or (hkl)	Phase Identification
1	35.50	(1010)	α, α'
2	38.40	(0002)	α, α'
3	39.30	(110)	β
4	40.20	(1011)	α, α'
5	63.15	(1120)	α, α'
6	70.70	(1013), (113)	α• α'• α''
7	74.45	(2020), (202)	∝ ຜ່→ ຜ"
8	76.40	(1122), (221)	α, α', α''
9	77.63	(2021)	α, α'
10	82.30	(0004)	α, α'
11	87.05	(2022)	α, α'
12	92.75	(1014), (114)	α, α', α"
13	102.70	(2023), (223)	α, α', α"
14	106.50	(2130), (240)	α, α', α''
15	109.60	(2131)	α, α'
16	114.70	(1124)	α, α'

Table 10: Experimental 20 (Bragg angles) values for samples heated to 1050° C $\frac{1}{2}$ hr. and furnace cooled to room temperature. Data taken at 22°C, CuK_{α} radiation.

Peak #	20 (deg)	(hkil) or (hkl)	Phase Identification
1	35.23	(1010)	α
2	38.56	(0002)	α
3	39.70	(110)	β
4	40.40	(1011)	α
5	53.23	(1012)	α
6	63.36	(1120)	α
7	70.80	(211)	β
8	76.52	(1122)	α
9	77.70	(2021)	α
10	82.40	(0004)	α
11	87.15	(2022)	α



Figure 35: Composite X-ray peaks; CuK_{α} radiation



Figure 36: Composite X-ray peaks; CuK_{α} radiation.

the lattice parameter of the beta phase we suggest that alpha double prime martensite formation in this alloy is influenced by the Mo in accordance with the proposed model discussed earlier (4). However, it must be mentioned that strong texturing has been observed in this alloy in the $<11\overline{2}0>$ direction and hence this factor must be taken into account when calculating the volume fraction of the phases formed.

From the model proposed by Mukherjee and Kato (4), the atom positions for the orthorhombic martensite are known. Based on these atom positions and the unit cell symmetry, forbidden reflections are calculated (56) (Appendix I). These calculated intensities matched very well with the X-ray diffraction experiments. The lattice parameters of the orthorhombic phase could also be calculated from this experiment and these were verified from electron diffraction patterns obtained as well. The lattice parameter value of the orthorhombic martensite phase calculated from the X-ray data are: a=3.04Å, b=4.94Å, c=4.64Å. The lattice parameter of the beta phase at room temperature was also calculated from the results obtained in figure 36. ($a_R=3.23$ Å)

4.3 Scanning Transmission Electron Microscopy

Some preliminary scanning transmission electron microscopy has been conducted on a select number of specimens. A typical alpha double prime martensite plate is shown in Figure 37. This micrograph corresponds to a sample held at 900°C. An analysis of a selected area diffraction pattern from a alpha double prime plate is shown in Figure 38. The spots obeyed the extinction rule corresponding to the atom positions of the alpha double prime unit cell as proposed by the model proposed by Mukherjee and Kato (4). The angles between the reciprocal lattice vectors shown in Figure 38 are 117° and 63°. If the diffraction pattern


Figure 37: STEM micrograph of sample 1050°C $\frac{1}{2}$ hour, 900°C lhour, water quenched.



Figure 38: Analysis of a SAD pattern from a region shown in figure 37. [001] zone axis.



Figure 39: Energy dispersive X-ray analysis from an orthorhombic martensite plate.

were from the alpha prime martensite or equilibrium alpha (both HCP) then these two angles should have been 120° and 60° respectively, as can be seen from Figure 11(a). A limited amount of microchemical analysis, using STEM has been done on the orthorhombic martensite plate. Figure 39 is a typical energy dispersive X-ray analysis data which demonstrates the feasibility of a detailed solute partitioning effect. At present there are some contaminants which we beleive are resulting from the specimen preparation techniques. Further it is surmised that the specimen thickness must be much smaller so that there is less of absorbtion of characteristics X-rays and the goal to identify solute partitioning is achieved in this alloy.

CHAPTER 5

SUMMARY AND CONCLUSIONS

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

- The X-ray diffraction experiments showed that alpha, alpha double prime, alpha prime and beta phases can be obtained in Ti 6211 after isothermal holding and quenching heat treatments.
- With decreasing temperatures of holding, the amount of precipitation of equilibrium alpha increases.
- 3. Samples heat treated in air showed more precipitation of equilibrium alpha consistent with the fact that oxygen in air is an alpha stabilizer.
- 4. At a certain temperature range (850°C-900°C) it has been found that the alpha double prime martensite formation from the parent beta phase is most favourable.
- 5. Molybdenum, which is a beta stabilizer and which decreases the lattice parameter of the beta phase is considered to be responsible for the formation of alpha double prime martensite.
- From X-ray diffraction technique, the lattice parameter of the following phases are determined.

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APPENDIX I Extinction rule for orthorhombic structure





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

11. 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 + $e^{(k/3 + L)}(e^{\pi i h} + e^{\pi i k})$](A-17)
from (II)
II.a. If h: even, k: even then $e^{\pi i h} + e^{\pi i k} = 2$
F = f[2 + $e^{(k/3 + L)}(2)$] from equation A-17
F = 2f (1 + $e^{\pi i (k/3 + L)})$.
Let $g_1 = k/3 + L$.
then F = 2f(1 + $e^{\pi i (g_1)}$
/F/² = $2^2 f^2(1 + e^{\pi i g_1})(1 + e^{-\pi i g_1})$
= $4f^2(1 + e^{\pi i g_1} + e^{-\pi i g_1})$
= $4f^2(2 + 2 \cos(\pi g_1))$
= $8f^2(1 + \cos^2(\pi g_1) - \dots (A-18)$
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 $g_1 = m + L$
If m + L = even and L (even), from equation A-18
/F/² = 16f² cos²(m/2 g_1) = 16 f² ($\frac{t}{2}$)² = $\frac{16f^2}{2}$.
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 f² cos²[m/2 . (m + L - 1/3)]
= 16 f² cos² [(m + L) - $\frac{m}{2} - \frac{m}{6}$

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+
$$16f^2 (\cos^{(m + L)} \cdot \frac{\pi}{2} \cos^{\pi}/6)^2 = 16f^2 \cos^2(\pi/6)$$

 $= 16f^2 \cdot (\pm \frac{3}{2})^2 = \underline{12f^2}$
II.a.4. If K = $3m - 1$, $g_1 = \frac{3m - 1}{3} + L = m + L - 1/3$.
 If m + L is odd, L (even) then from equation A-18
 $/F/^2 = 16f^2 \cos^2(\pi/2 \cdot m + L - \pi/6)$
 $= 16f^2 (\sin m + L \cdot \pi/2 \sin \pi/6)^2$
 $= 16f^2 (\pm 1)^2 = \frac{4f^2}{3m + 1} + \frac{1}{3}$
 II.a.5. If K = $3m + 1$, $g_1 = \frac{3m + 1}{3} + \frac{1}{2}$
 $g_1 = m + L + 1/3$, if m + L is even (Lodd)
 $/F/^2 = 16f^2 \cos^2(\frac{\pi}{2} \cdot (m + L) + \pi/6)$.
 $= 16f^2 (\cos(\frac{\pi}{2} (m + L) \cos \pi/6)^2$
 same as II.a.3.
 II.a.6. If k = $3m-1$, $g = \frac{3m - 1}{3} + L = m + L - 1/3$
 If m + L is odd, (L even)
 $/F/^2 = 16f^2 \cos^2(\pi/2 \cdot m + L - \pi/6)$.
 $= 16f^2 (\sin m + L \cdot \pi/2 \sin \pi/6)^2$
 same as II.a.4.

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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 = $3m \pm 1$ and L is odd $/F/^2 = 12f^2$ if $k = 3m \pm 1$ 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 $g_1 = k/3 + L$ $F = 2f(1 - e^{\pi i g})$ $/F/^{2} = 4f^{2}(1 - e^{\pi i g_{1}}) (1 - e^{-\pi i g_{1}})$ $= 4f^{2}(1 - e^{\pi i g L} - e^{-\pi i g L} + 1)$ = $4f^2(2 - 2\cos(\pi g_1))$ $= 8f^{2}(1 - \cos(\pi g_{1}))$ = $8f^2 \cdot 2 \sin^2(\pi/2 \cdot g_1) = 16f^2 \sin^2(\pi/2 \cdot g_1) \dots \dots \dots \dots \dots (A-19)$ II.b.l. If k = 3m, then $g_1 = m + L$ If m + L is odd (and L even) equation A-19 becomes $/F/^2 = 16f^2 \sin^2(\pi/2 \cdot m + L)$ $= 16f^2 (^+_{-1})^2 = \underline{16f^2}.$ 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)
 $/F/^2 = 16f^2 (\sin^m + L)\pi/2 \cos \pi/6)^2$
 $= 16f^2 (\frac{4}{\sqrt{3}})^2 = 12f^2$
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)
 $/F/^2 = 16f^2 [-\cos (m + L) \pi/2 \sin \pi/6]^2$
 $= 16f^2(\frac{4}{2})^2 = 4f^2$
II.b.5. If k = 3m + 1 then $g_1 = m + L + 1/3$
from equation A-19
 $/F/^2 = 16f^2 \cos^2[\pi/2(m + L) + \pi/6]$
If m + L is even (L even)
 $/F/^2 = 16f^2 (\sin^2[\pi/2(m + L)] \sin \pi/6]^2$
 $= 16f^2 (\frac{4}{2})^2 = 4f^2$ 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 $/F/^2 = 16f^2 (\sin \pi/2(m + L) \cos \pi/6)^2$
 $= 16f^2 (\frac{4}{3})^2 = 12f^2$ same as II.b.3.

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 = $12f^2$