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**PHASE IDENTIFICATION AND
CHARACTERISATION OF TITANIUM-6211**

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Krishnan Narasimhan

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of the requirements for

Masters degree in Metallurgy

A handwritten signature in dark ink, appearing to read "K. Mukherjee".

Major professor

Kali Mukherjee

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PHASE IDENTIFICATION
AND
CHARACTERISATION OF TI-6211

Krishnan Narasimhan

A THESIS

Submitted to
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ABSTRACT

PHASE IDENTIFICATION AND CHARACTERISATION IN A Ti-6WT%Al-2WT%Nb-1WT%Ta-1WT%Mo ALLOY: MORPHOLOGY, CRYSTAL STRUCTURE AND SOLUTE PARTITIONING

By

Krishnan Narasimhan

The purpose of this investigation was to determine the nature, morphology and crystallography of various phases present in Ti 6211 as a consequence of various isothermal holding temperatures in the alpha + beta range. Solute partitioning studies were conducted using Scanning Transmission Electron Microscope and energy dispersive analysis to determine the nature of elements stabilising the various phases detected at a particular isothermal holding temperature. The phenomenon of ordering in Ti 6211 was investigated and evidence has been presented regarding the formation of an ordered phase after aging at 450°C for seventy two hours. TEM techniques have been used to establish the crystal structure of various phases present at a particular isothermal holding temperature.

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1. INTRODUCTION

The use of Titanium alloys in structural applications is undergoing continuous expansion and such an expansion results in the requirement for alloys which have wider ranges of properties and whose properties can be tailored to fulfill the requirements of a specific application. Titanium 6211 (Ti-6Al-2Nb-1Ta-1Mo) is such an alloy which has recently gained attention for many applications. This is primarily an alpha alloy with some amount of beta. A comprehensive research program was initiated to develop a better understanding of the effects of composition and microstructure on the structure related properties of titanium alloys with emphasis on Ti-6211. Though the knowledge of the physical metallurgy and fracture mechanics of titanium alloys has advanced considerably during the last four decades, several technical issues with regard to this alloy have remained unclear. The extent of interest in the microstructure of Ti-6211 has been propelled by the fact that the mechanical properties like strength, ductility, and fracture toughness are strongly influenced by the microstructure. It is believed that fracture toughness can be improved by raising the solution temperature to produce a microstructure with coarse widmanstatten alpha transformed from beta. In addition to good mechanical properties, Ti-6211 has good resistance to corrosion. A host of microstructural features

can be produced depending upon the hot working conditions, heat treatment, and variations in quenching and cooling rates. In such a two phase alloy the martensitic transformation is influenced by the chemistry of beta phase from which the martensite is derived. The beta phase (b.c.c.) of titanium alloys can transform martensitically into several crystallographic forms:

- 1) α' (h.c.p.) martensite
- 2) α'' (orthorhombic) martensite
- 3) face centered orthorhombic martensite
- 4) face centered cubic martensite (observed only in thin films [1])

The stability of the β -phase and the crystallography of the martensite are related to the solute enrichment of the beta phase. Whereas the martensitic transformation in a single phase austenite is with an unique habit plane and crystal structure, the martensitic transformation in an alpha + beta alloy can manifest variations in crystallography and transformation kinetics depending on the solute partitioning between the two phases. Stress induced martensite can occur [2] if a metastable beta phase exists in the alloy as a consequence of rapid cooling or a supersaturation of a beta phase with beta stabilising elements at the solution treatment temperature. The present investigation is concerned with the detection of various phases present as a function of isothermal heat treatment at various temperatures within the alpha + beta phase field. Electron beam microprobe, and

energy dispersive microanalysis, by using high resolution STEM have been used to determine the relative ratios of alpha and beta stabilisers within the phases obtained after a given heat treatment. Phase identification, morphology, and solute partitioning in this alloy are discussed in this thesis.

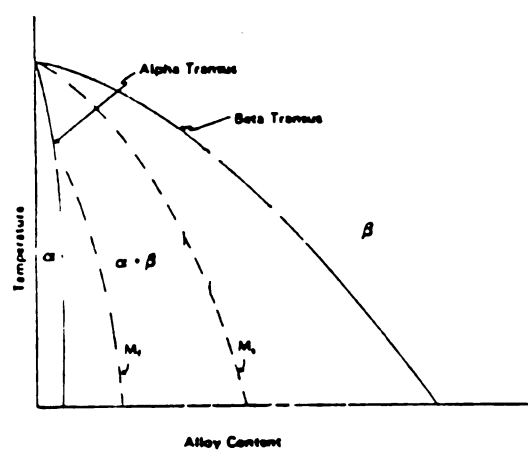


Fig.1. Partial Phase Diagram of the Beta Isomorphous System.

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

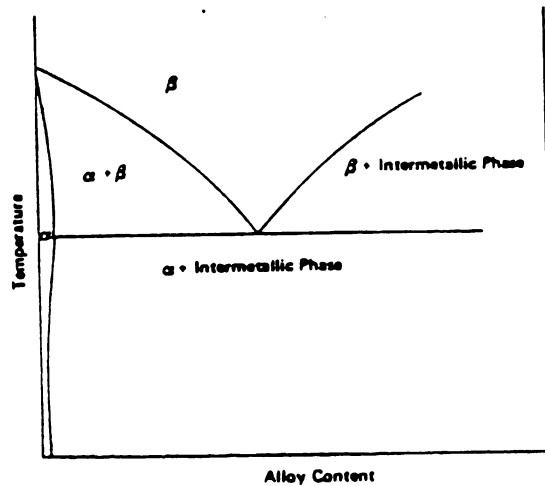


Fig.2. Partial Phase Diagram of the Beta Eutectoid System.

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

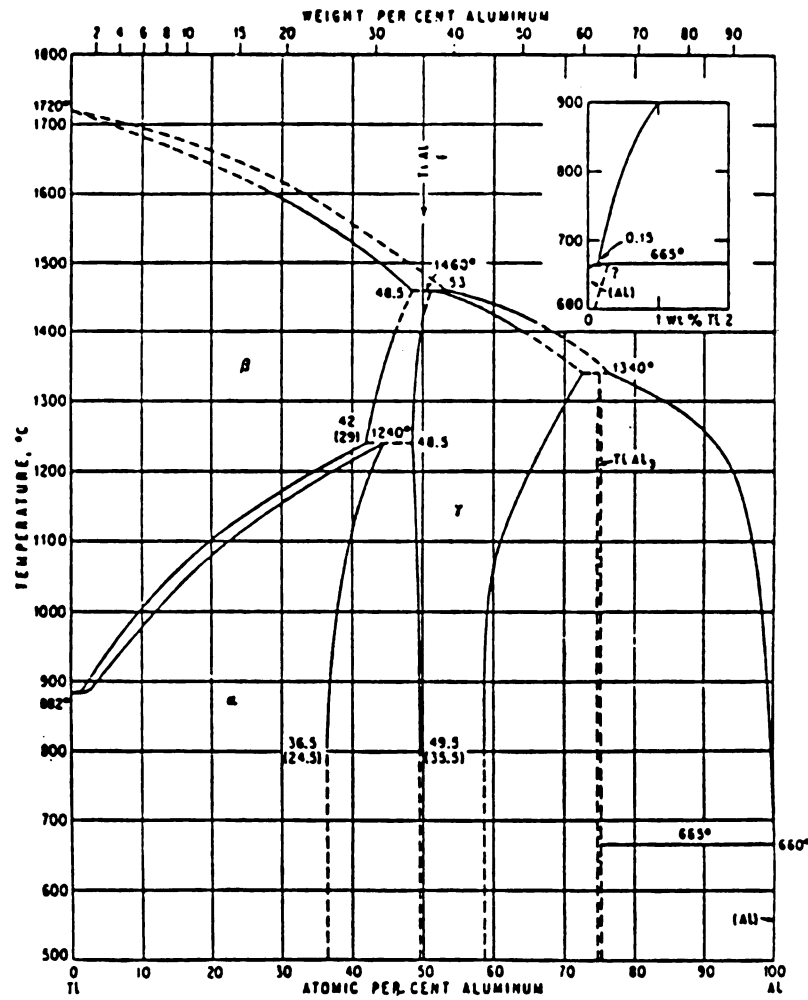


Fig.3. Constitutional diagram of titanium-aluminum system.

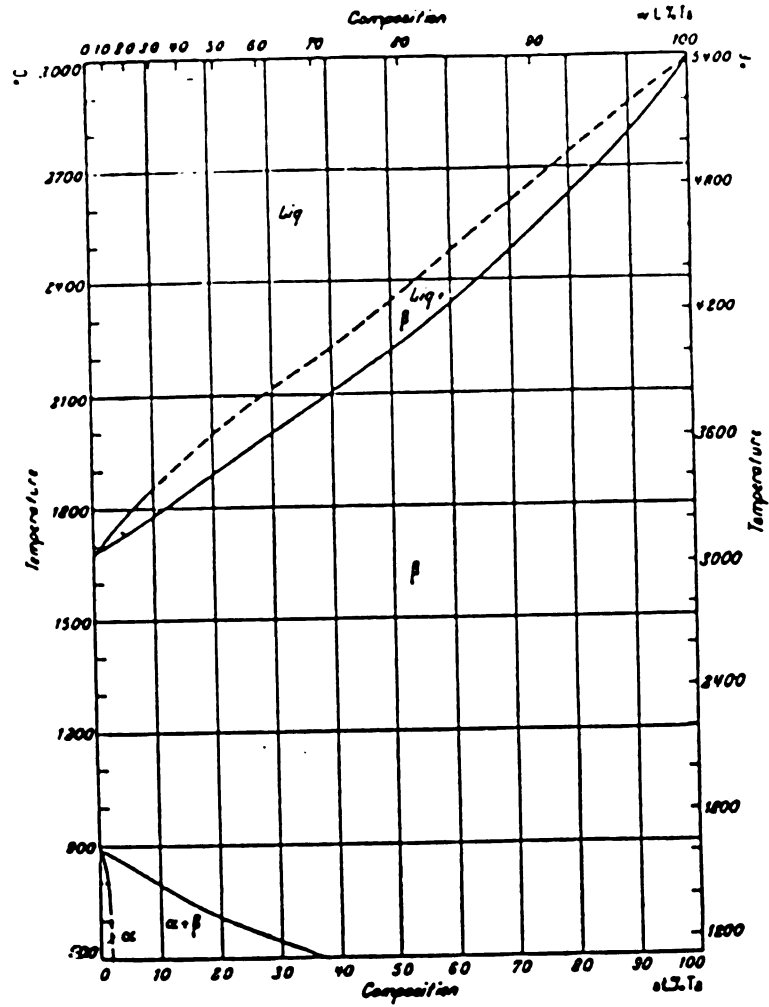


Fig.4.

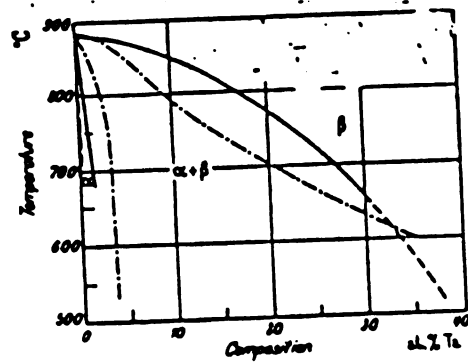


Fig.5. Constitutional diagram of titanium-tantalum system.

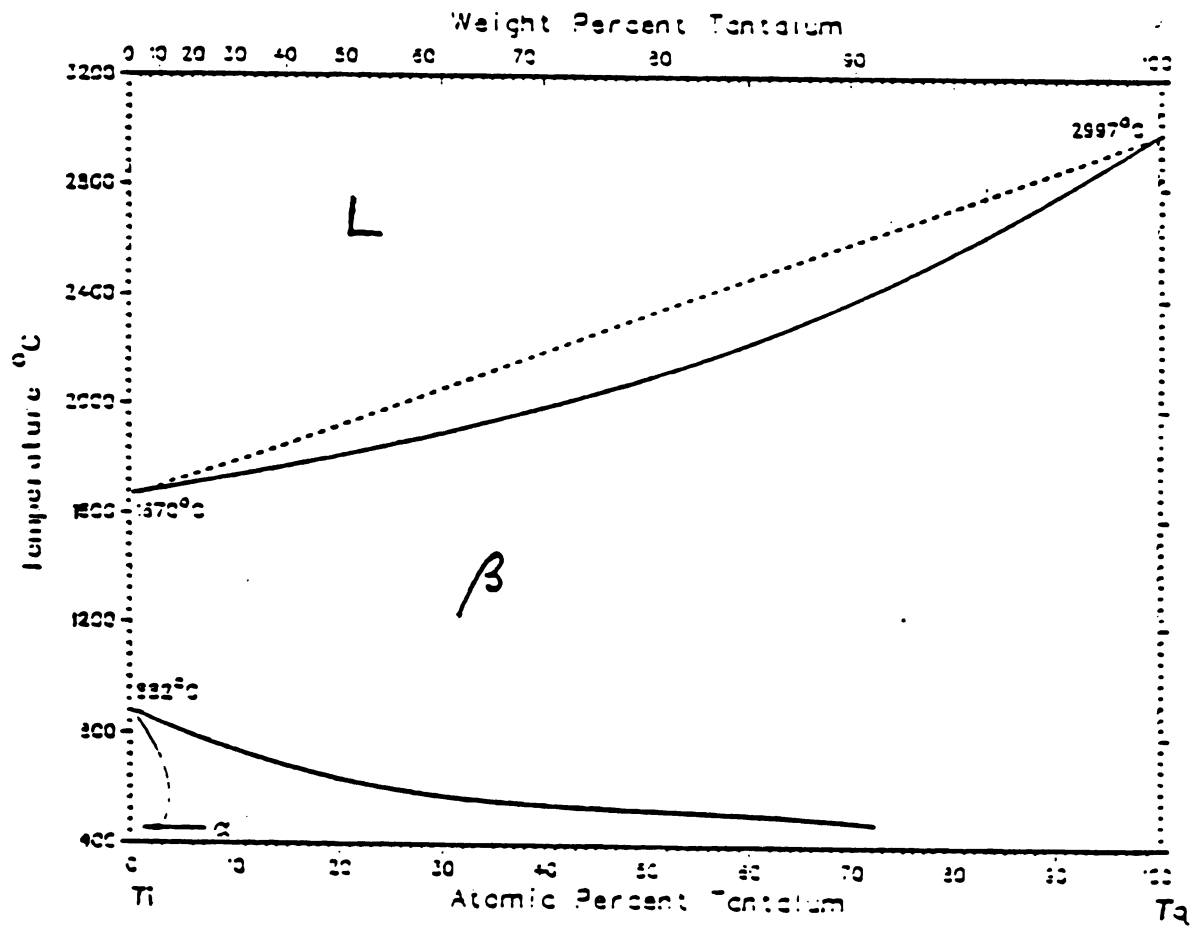


Fig.6. Ti-Ta Phase Diagram

2. REVIEW OF PREVIOUS STUDIES

Titanium alloys are broadly classified into alpha titanium, beta titanium and alpha + beta titanium, depending on the alloying elements present in the alloy. Elements like Al, Ge, Ga, C, O and N stabilise alpha i.e. in the region where alpha and beta coexist, these elements are more soluble in alpha than in beta. Beta titanium alloys have predominantly beta stabilising elements like V, Mo, Ta, Nb etc which are completely miscible with the beta phase, or elements like Mn, Fe, Cr, Co, Ni, Cu, Si (beta eutectoid elements) which transform beta phase into alpha and an intermetallic phase. Fig. 1 and 2 illustrate the above mentioned categories. Ti-6211 has 6.0 w/o aluminum, 2.0 w/o niobium, 1.0 w/o tantalum and 0.8 w/o molybdenum. Aluminum is an ' α ' stabiliser and the rest are beta stabilisers. Figs 3-6 illustrate the phase diagrams of these elements when alloyed with titanium. Two other elements zirconium and tin have the same extent of solubility in both alpha and beta and are essentially strengthening agents.

2.1 Phase Transformations in Titanium Alloys

Phase transformations occurring in titanium alloys can be classified into eight groups after Murakami [3]

1. Decomposition of beta phase when quenched to produce alpha prime, alpha double prime, athermal omega, retained beta.

2. Metastable beta transforming isothermally to isothermal omega, alpha double prime, beta prime, alpha, α_2 , β_2 .
3. Decomposition of retained beta leading to isothermal omega, beta prime, widmanstatten alpha, raft alpha, α_2 , β_2 , stress induced martensite, isothermal martensite.
4. Decomposition of martensite producing alpha, intermetallic compound, and beta.
5. Formation of alpha phase from omega, and from beta.
6. Eutectoid decomposition.
7. Precipitation from alpha producing ordered phase ' α_2 '.
8. Formation of interface phase.

2.1.1 Martensites in Titanium Alloy

High temperature b.c.c. phase termed ' β ' transforms martensitically during quenching, which can be classified as hexagonal martensite [4, 5], face centered cubic martensite, orthorhombic martensite [6] and face centered orthorhombic martensite [7]. α' martensite (hexagonal) is the most prevalent martensite. Two morphologies of the same have been observed 8 massive martensite and acicular martensite [9,] [10]. The massive martensite has colonies which can be resolved optically, exhibits surface relief effects from plates within the colonies. The boundaries between the plates have been shown to consist of walls of dislocations, whereas the interior of the plates contain a relatively dense tangle of dislocations. Massive martensites have also been called packet or lath martensites. With increase in solute concentration, the massive martensite colony size decreases, and

at a specific solute concentration (which depends on the alloy systems) the colonies become individual plates. These plates have an acicular morphology. This martensite is frequently internally twinned on $\{10\bar{1}1\}_{\alpha'}$. Habit plane determinations on the acicular martensite have been performed and these martensites have, for the most part, the $\{3\bar{3}4\}_{\beta}$ habit plane [11, 12] which is predicted by the Bowles and McKenzie's crystallographic theory of martensite.

The second type of titanium martensite (α'') has an orthorhombic structure. This structure was first discovered by Bagariatskii in 1959 who reported it on the basis of X-ray diffraction. This martensite occurs in some binary alloys, eg Ti-Mo, Ti-Nb, Ti-W, Ti-Re, and has been also observed in Ti-6Al-2Sn-4Zr-6Mo accompanied by a reduction in ductility [13]. The lattice parameters of orthorhombic martensite are strongly composition dependent. Characteristic pattern reveals five low angle lines compared to three for hexagonal martensite. Orthorhombic martensite has been examined in the electron microscope in a Ti-8.5 Mo-0.5 Si alloy and has been found to be internally twinned on $\{111\}_0$ planes [14].

Several workers have observed a face centred cubic martensite in Ti-Fe [15], Ti-Cr [16] etc. This martensite has always been reported on the basis of thin foil electron microscopy evidence. Recent evidence obtained by Williams and Rhodes showed that this martensite is orthorhombic in its bulk form [17]. Strong evidence as a consequence of work done by several investigators indicates that the face centred

cubic and face centered tetragonal martensites reported on the basis of thin foil electron microscopy, are thin foil artifacts and are probably a thin foil version of a bulk orthorhombic martensite.

Apart from athermal type of titanium martensites, martensite forms during stressing in metastable bcc Ti alloys. There is evidence of mechanical twinning [18, 19] in some alloys, and it is suggested that the concentration and the type of solute has an important influence on whether the stress-induced product in a given alloy is twinning or martensite. Electron microscopy of Ti-11.5Mo-4.5Sn-6Zr; Ti-14Mo-3Al [20, 21] showed bcc twins. There is enough evidence to show that other alloys do form stress induced martensite and in these cases the martensite product is orthorhombic. Difficulties due to line broadening as a result of straining, such as poor resolution, led to a study by Williams [21], who reported that hexagonal stress induced martensite in different alloy compositions could not be reproduced, but instead revealed orthorhombic alpha double prime phase. It has been suggested that aluminum additions to Ti-Mo and Ti-V alloys promote stress induced α'' . Some β -Ti alloys were reported to have fcc stress induced martensite product [22], and hcp martensite [23].

2.1.2 Martensite Crystallography

Several workers have tried to explain the crystallography of martensites α' and α'' with respect to the parent phase beta. Oka and Taniguchi [24] suggested that Mo content

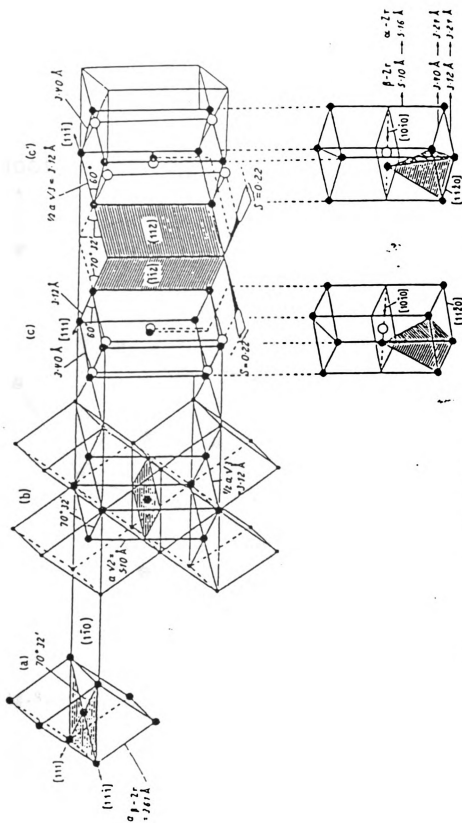


Fig. 7. Illustration of mechanism proposed by Burgers for transformation of body-centered cubic lattice to hexagonal close-packed lattice in zirconium, after (14).

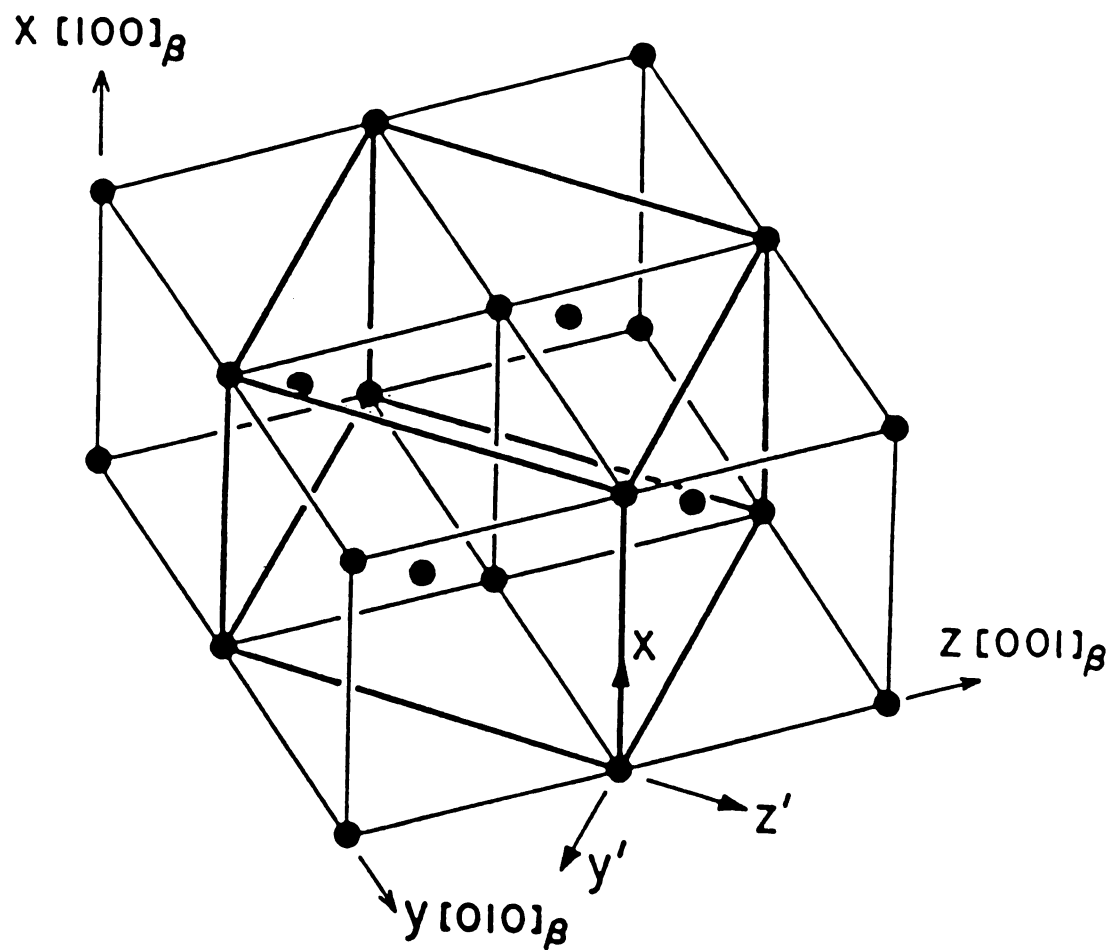


Fig.8. Lattice correspondence of martensites showing the four unit cells of the BCC crystal and its face centered tetragonal equivalent.

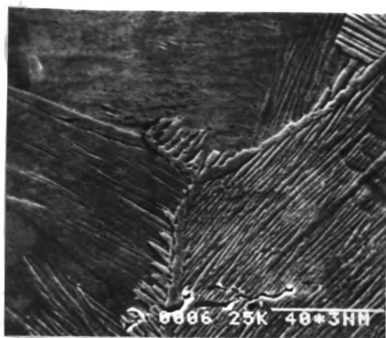


Fig (9). SEM micrograph of 700°C specimen showing
widmanstatten alpha

influenced the lattice parameter of stress induced orthorhombic phase to approach that of the beta phase. Sasano et al. [25] confirmed that with increasing beta stabilising agent the crystal structure of Ti martensite changes from hcp to orthorhombic. Fig. 7 illustrates the Burger's mechanism for the beta (bcc)—alpha prime (hcp) transformation in Ti-alloys [26]. Mukherjee and Kato [27] suggested that all the titanium martensites can be generated from a face centered tetragonal equivalent of the four unit cells of the bcc beta phase (Fig 8). In the transformation of beta — alpha prime or alpha double prime, it was suggested [27] that for alpha prime, the Bain strain is brought about by Burger's mechanism where the operation of the $\{112\} \langle 111 \rangle_{\beta}$ 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 shuffling on every other (011) plane is necessary to create the hcp structure. In the formation of alpha double prime martensite, after the operation of the $\{112\} \langle 111 \rangle_{\beta}$ shears, the $(011)_{\beta}$ plane does not completely change into the hexagonal close packed plane but stops midway between the $(011)_{\beta}$ and $(0001)_{\alpha}'$ leaving the angles θ_1 and θ_2 different from 120° . Thus according to Mukherjee and Kato the alpha double prime martensite can be considered a distorted alpha prime martensite. In f.c.o. martensite there is no shuffling and lattice correspondence is very similar to Au-Cd martensite. From the Bain strains calculated in Ti-12.6V by Mukherjee and Kato [27] for the

f.c.o. martensite it is obvious that f.c.o. martensite cannot be considered a distorted alpha prime martensite. Recently Sircar, Krishnan, Mukherjee [28] showed that the lattice parameter of the beta-phase at the M_s temperature is a dominant factor which determines the stability of the beta-phase and/or the type of martensitic transformation in Ti-6211 alloy. The magnitudes and signs of the Bain-strain associated with the martensitic transformations are directly related to the beta-phase lattice parameter. From theoretical analysis it was suggested that those beta stabilising elements which reduce the unit cell size of the beta phase, tend to favour the α'' martensite. Mukherjee and Kato [27] have also shown by strain energy minimization criteria and by Bain strain calculation, that there exists a critical Bain strain at which a transition from α' martensite to α'' martensite is favourable. This reveals the fact that the transformation of beta — alpha double prime is more favourable than beta — alpha single prime for certain critical solute concentration of the beta phase. Of the various alloying elements in Ti-6211 molybdenum produces a contraction in the beta lattice parameter and thus tends to favor the alpha double prime martensite formation.

2.1.3 Omega Phase

Beta phase in titanium alloys when retained in metastable form by quenching, can partially decompose during quenching into another metastable precipitate known as the athermal omega phase [29]. Such alloys which tend to

decompose to " ω " phase contain a sufficient concentration of beta stabilising elements to depress the martensite finish temperature beneath room temperature. There is a very limited composition range over which omega phase (athermal) occurs, and the extent depends on the particular alloy system under consideration. There is enough evidence to suggest that athermal omega forms without a change in composition. The structure of the omega phase is not cubic as suggested by Frost et al. [30], however it is less clear whether the phase is hexagonal as claimed by Silcock [31] or trigonal symmetry as claimed by Bagariatskii [32]. Athermal omega was considered for sometime to form by a martensitic transformation largely because its formation cannot be suppressed by quenching. TEM studies have shown that athermal omega occurs as extremely small particles ($20-40\text{\AA}$) with a very high density. De Fontaine [33] proposed a model for the formation of omega phase based on displacement controlled mechanism. ' ω ' lattice can be generated from the beta phase by a series of $2/3 \langle 111 \rangle$ longitudinal displacements. Further, Paton, de Fontaine and Williams [34] have used cold stage transmission electron microscopy to show that the omega phase can be reversibly formed on cooling beneath room temperature. Such reversibility is consistent with a displacement controlled transformation which can occur without change in composition. This mechanism also explains the complex diffuse intensity of diffraction observed in metastable beta alloys. The streaking in electron

diffraction pattern has been attributed 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. Sass [35] has suggested that the diffuse intensity results from coherent scattering from rows of athermal omega phase particles resulting in sheets of intensity lying normal to $\langle 111 \rangle$. It has been reported that variations in oxygen content of the alloy has a direct bearing on the apparent composition limit at which sharp or well defined omega phase reflection maximum can occur, leading to a disagreement amongst various workers regarding the composition at which athermal omega can be suppressed. Another observation made is the case with which alpha nucleates from unstable beta when there is a presence of intermediate unstable products like " ω ".

In addition to athermal omega, isothermal omega can also form as a metastable transition precipitate in alloys of intermediate concentration of beta stabiliser during aging at temperatures up to 550°C . This phase was originally discovered in 1954 by Frost et al. [36]. Isothermal beta — omega transformation occurs most rapidly of all beta phase decomposition modes, and the rapid kinetics of omega phase formation are related to the case with which the hexagonal omega phase can be formed from the bcc lattice. Isothermal omega forms during aging as coherent [37] precipitates of small size and high particle density [38, 39]. Ellipsoidal [40] and cuboidal [41] omega phase morphologies have been

observed in titanium alloys, the morphology being controlled by the misfit between the omega precipitate and the bcc matrix. Ellipsoidal omega phase occurs in low misfit alloys like Ti-Mo, Ti-Ta, Ti-Nb, the long axes of the ellipsoids of revolution lying parallel to a $\langle 111 \rangle_\beta$ direction. Cuboidal omega phase is observed in high misfit alloys such as Ti-Fe, Ti-V, Ti-Cr, Ti-Ni, Ti-Mn. The cuboids form with their cube faces parallel to $\{100\}_\beta$ planes [42]. Ternary additions like Al, Zr, Sn influence the formation and stability of omega phase. Studies have shown [43] that the principal influence of aluminum on the stability of omega phase is to promote separate nucleation and growth of alpha phase after relatively short aging times; this alpha phase grows and consumes the $\beta + \omega$ matrix, limiting the time temperature range over which omega exists. Sn, or Zr additions reduce the volume fraction of omega and stabilise the beta phase. Such ternary additions reduce the maximum temperature of stability of the omega phase and thus they are used to promote omega — alpha transformation. Oxygen also influences omega formation and stability by slowing down the kinetics of its formation and reducing the volume fraction of omega phase formed. Limited data suggests that oxygen tends to increase the stability of the beta phase and does not significantly promote the independent nucleation of alpha phase.

2.1.4 Alpha Phase Formation

Equilibrium alpha phase in titanium alloys can be formed from the metastable beta phase, omega phase, β' -phase, or

during the decomposition of titanium martensites on tempering. Morphology and distribution of alpha phase depends on the alloy content and in the manner in which it forms. On continued aging of alloys which have undergone the $\beta + \beta'$ phase separation reaction, alpha phase can be nucleated within the β' regions and can either grow as "rafts" of random shape which contain a large number of very small particles, or as well defined needles which grow with their long dimension parallel to $\{110\}_{\beta}$ plane [44]. Alpha phase can be nucleated directly from the metastable beta phase in concentrated alloys aged above the maximum temperature for β' formation. In such cases two types of alpha phases are observed, these type being different in morphology and crystallography [45]. The first type of alpha phase known as Widmanstatten alpha forms as plates and needles, the long axes of which lies parallel to $\{110\}_{\beta}$. This type of alpha phase forms with the characteristic Burgers orientation relation, with each Widmanstatten plate is a single variant of the Burgers orientation relation. This type of alpha is observed in binary alloys linear in beta stabiliser and in alloys which contain a good amount of aluminum eg. Ti-6Al-4V. Recently Sircar, Krishnan, Mukherjee [28] have shown the occurrence of prominent Widmanstatten alpha plates in Ti-6211 Fig (9). Typical basket weave alpha structure, and blocky spagetti alpha have also been observed in this alloy [28].

The second type of alpha phase occurs frequently in binary alloys with a high concentration of beta stabilising

elements eg: Ti-18 wt % Mo, Ti-8Mo-8V-3Al [46]. This alpha is known to form as aggregates of very small particles, and two distinct morphologies of this type have been observed, one assuming a long lenticular shape and the other raft and patchy. Selected area diffraction techniques have shown that the orientation relation between the alpha phase and the beta matrix is not the commonly observed Burger's relationship. Alpha regions contain alpha particles from more than one variant of the orientation relation, suggesting that sympathetic nucleation [47] is involved in the process. In alloys aged at temperatures which result in direct formation of the alpha phase, the distribution of the alpha phase is inhomogeneous and plate size is coarse. This results in large sections of untransformed beta phase between the coarse alpha platelets, leading to a low tensile ductility in this alloy. Such a deleterious distribution can be improved by deformation prior to aging, because such a deformation introduces a high dislocation density from which alpha can nucleate homogeneously, leading to enhancement of properties in beta phase alloys.

2.1.5 β' Formation

In titanium alloys the bcc phase can separate into two bcc phases of different composition. This composition reaction was originally termed $\beta_1 + \beta_2$ by some workers. It is proposed that the mixture of bcc phases resulting from the phase separation be called $(\beta + \beta')$. The β' -phase occurs as uniformly distributed, coherent bcc zones in the beta phase

matrix, in the range of 200-500°C temperature. The morphology of the β' regions is variable and appears to depend on the composition difference and misfit between the two bcc phases [48]. The occurrence of β' has been observed in a wide range of alloy systems where sufficient beta stabilisers preclude omega phase formation during low temperature aging. The phase separation is thus viewed as a kinetically favorable mode of beta phase decomposition in alloys where direct formation of the equilibrium alpha phase is sluggish and omega phase cannot be formed. The detection of β' precipitates has so far been possible by thin foil electron microscopy only because X-ray diffraction led to peak broadening. The composition of β' have not been determined directly. However, on continued aging, the equilibrium alpha phase precipitates within the β' regions, revealing the fact that β' is solute lean. The thermodynamics of the phase separation reaction have been considered by several workers, in particular Kauffman and Bernstein [49] who seem to agree that the reaction requires an inflected beta phase free energy composition curve, and that β' is a metastable constituent. The stability and kinetics of formation of the β' precipitates depend on the alloy composition. The addition of ternary elements which promote alpha nucleation i.e. oxygen and aluminum reduce the time and stability of the β' precipitates by accelerating the rate at which alpha phase is nucleated. One interesting aspect of this transformation is that the $\beta + \beta'$ reaction followed by

the β' — alpha reaction appears to be a promising means of producing a uniform dispersion of alpha hardening precipitates in beta alloys, especially for deep hardening applications.

2.1.6 α_2 Formation

In alloy systems which exhibit an increasing solid solubility in the alpha phase with increasing temperature, it is possible to produce a supersaturated solid solution which will subsequently undergo alpha decomposition during aging. Several eutectoid alloys exhibit extensive solid solubility and in these the alpha phase can precipitate the intermetallic compound on aging below the eutectoid temperature. In two of these systems, Ti-Si and Ti-Cu, significant supersaturation can be achieved by quenching from under the eutectoid temperature. The other important class of alloys in which significant supersaturation can be achieved are alloys between Ti and group III or group IV elements, notably Al, Ga, In, Sn and Pb. All of these alloys decompose during aging to form an ordered phase designated α_2 ; this phase is based on the composition Ti_3X and has a DO_{19} structure. The mode of formation of the α_2 phase depends on the alloy system under consideration, however in Ti-Al alloys, the phase forms as a uniform dispersion of coherent precipitates. As the α_2 particle size increases, either by coarsening in dilute alloys or by aging at high temperatures in concentrated alloys, the α_2 precipitates assume an elongated ellipsoidal morphology, the direction of elongation being $[0001]_\alpha$ 50 presumably because the alpha/ α_2 misfit is smaller in the τ

direction. The aspect ratio of the precipitates can be altered in Ti-Al alloys containing ternary additions of Ga and Sn since these two alloying elements have the opposite effect on the τ and $\bar{a}$ direction misfits of the α_2 phase [51]. In Ti-Al-Sn alloys the α_2 phase is nearly equiaxed and in Ti-Al-Ga alloys the α_2 phase grows out as extended rods. Considerable dispute existed between workers regarding the extent and shape of the α_2 phase field on the Ti-Al phase diagram. Crossleys diagram shows that the Ti_3Al phase exists only as a stoichiometric line compound, whereas Blackburn's diagram shows that the α_2 phase exists as a single phase over a wide range of composition. It has been suggested by Williams that the shape of the α_2 phase in Blackburn's diagram is correct because existence of an extensive α_2 phase field has been confirmed. Blackburn's diagram Fig (10) indicates that there is a anomalous contrast representing the limiting aluminum concentration at which the single phase α_2 structure exists. Blackburn suggested that the anomalous phase contrast may be due to excess Ti atoms in the antiphase boundaries, or due to a very thin layer of disordered material.

Increasing amounts of ternary alloying elements lead to a reduction of the volume fraction of the ordered α_2 -phase in quenched alloys [54]. This effect is understood qualitatively if it is clear that these elements all lower the M_s temperature of titanium alloys. In addition to an influence on α_2 volume fraction, alloys that contain 5% at Nb also

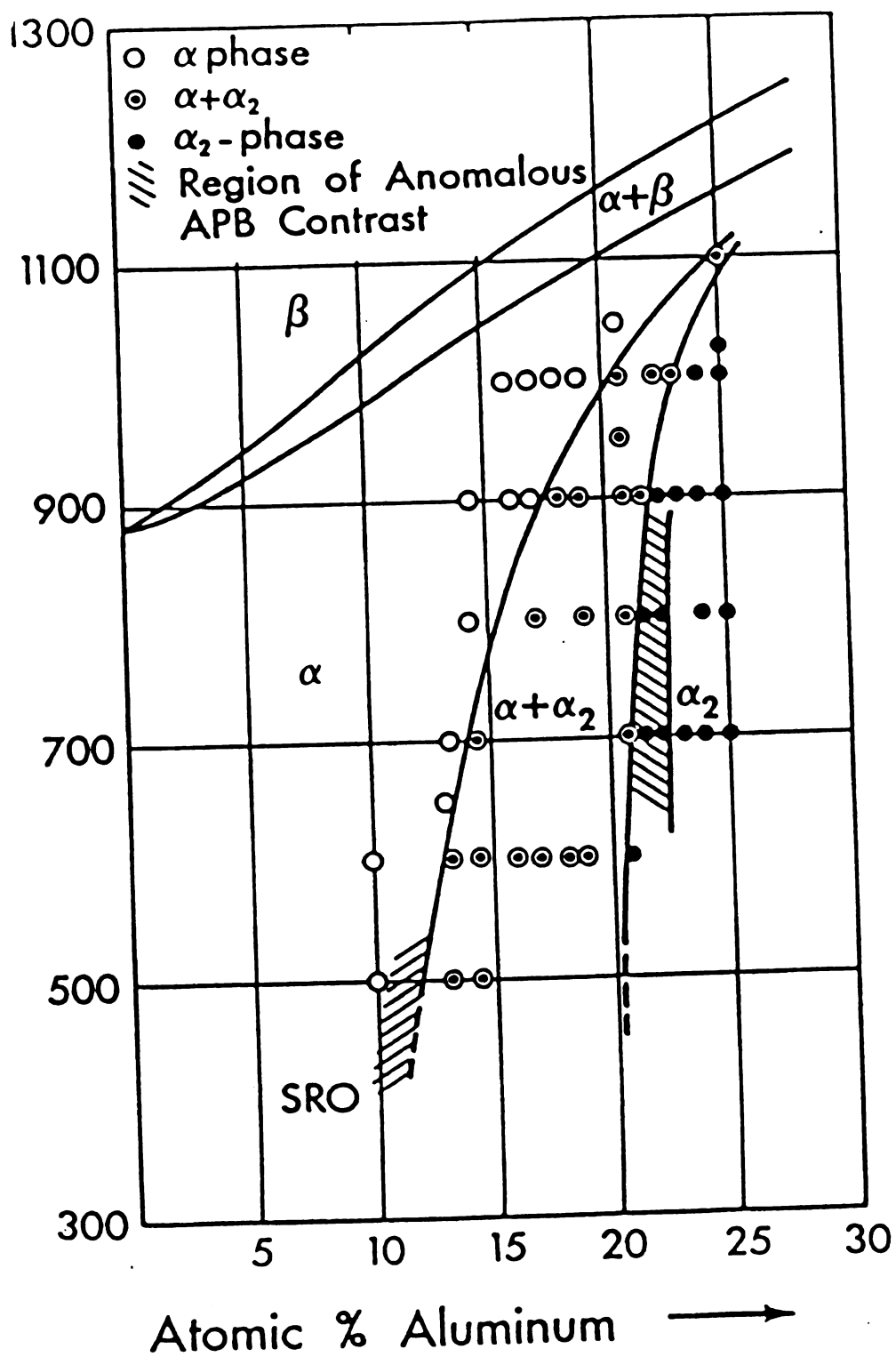


Fig.10.

exhibit recrystallisation reaction. The recrystallisation reaction frequently is initiated at prior beta grain boundaries, possibly because such sites are a good source of the disordered boundary which surrounds the recrystallised regions.

Recently Namboodri [55] suggested a shifting of the $\alpha-(\alpha+\alpha_2)$ transition point to lower aluminum concentrations and to higher temperatures than those proposed by Blackburn. Regions of short range order were determined by electrical resistivity measurements. Namboodri et al. [55] investigated the decomposition behaviour of the alpha phase in the Ti-Al system containing up to 19 at % Al (11.8 wt % Al). Isochronal and isothermal resistivity changes were measured in alloys originally quenched from temperatures above the $\alpha-(\alpha+\alpha_2)$ transition point. Precipitation of the ordered α_2 phase followed typical precipitation kinetics and resulted in a decrease in the as quenched electrical resistivity of the alloys. Short range ordering raised the resistivity of quenched alloys, and the plastic deformation of short range alloys (ordered) led to decreases in the electrical resistivity. On the basis of these studies, Namboodhiri et al suggested that the $\alpha-(\alpha-\alpha_2)$ boundary should be shifted to lower aluminum concentrations than those proposed by Blackburn. Recently, R. D. Shull, et al. [56] have identified the presence of α_2 (ordered Ti_3Al type) in Ti-6211 alloy. Till this data the presence of α_2 in titanium 6211 has not been unequivocally established. The fact that α_2

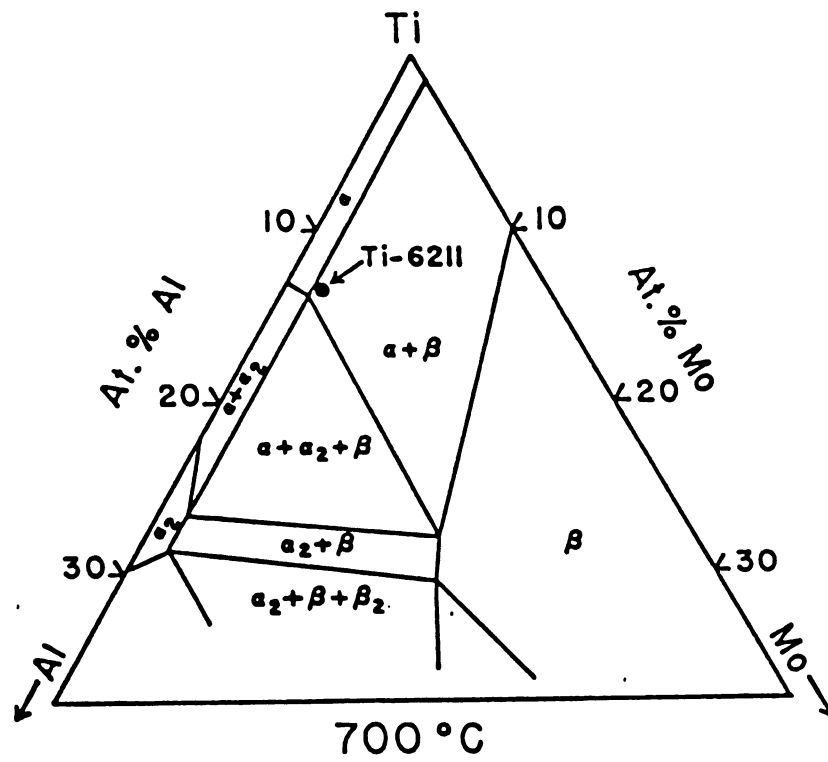


Fig.11. Ti-rich corner of the Ti-Al-Mo phase diagram at 700°C.

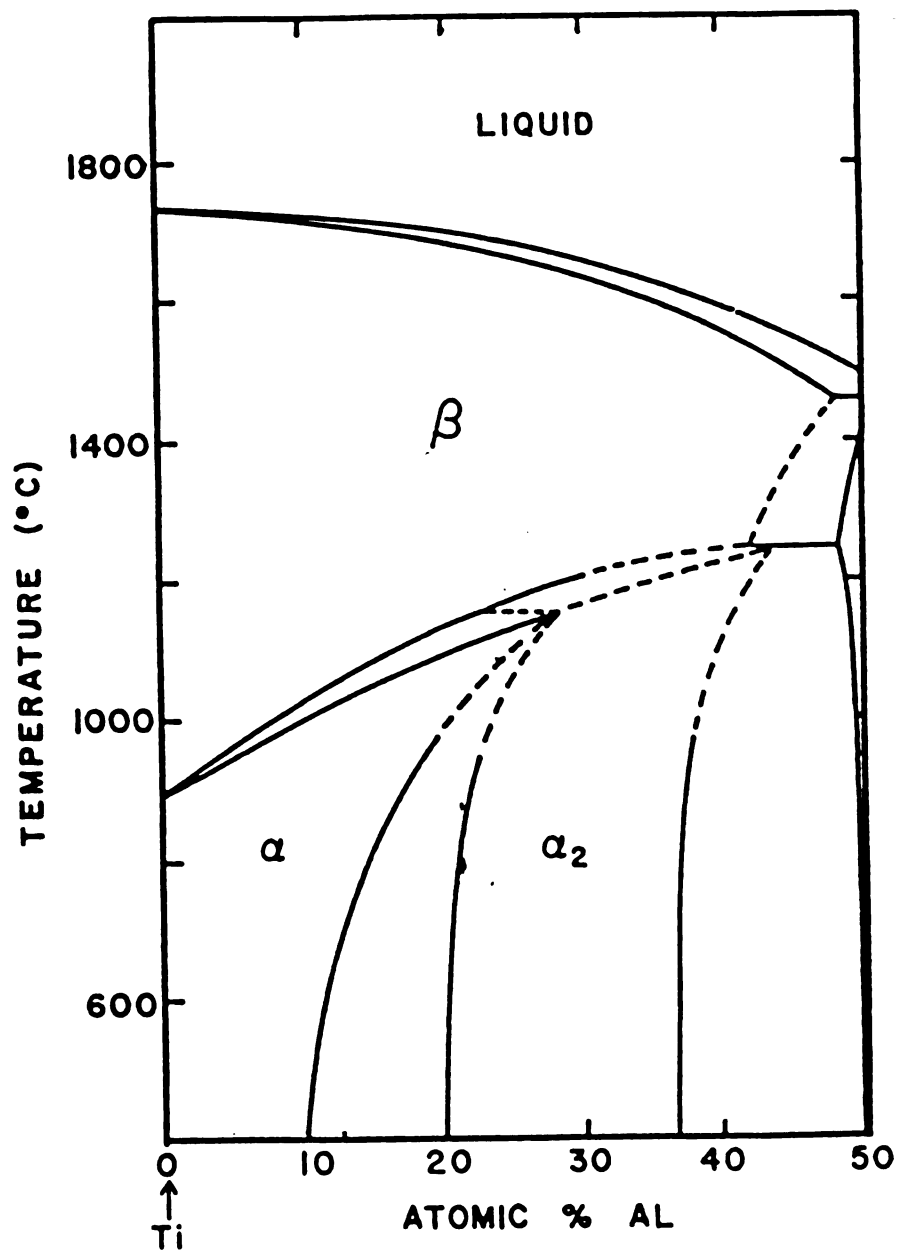
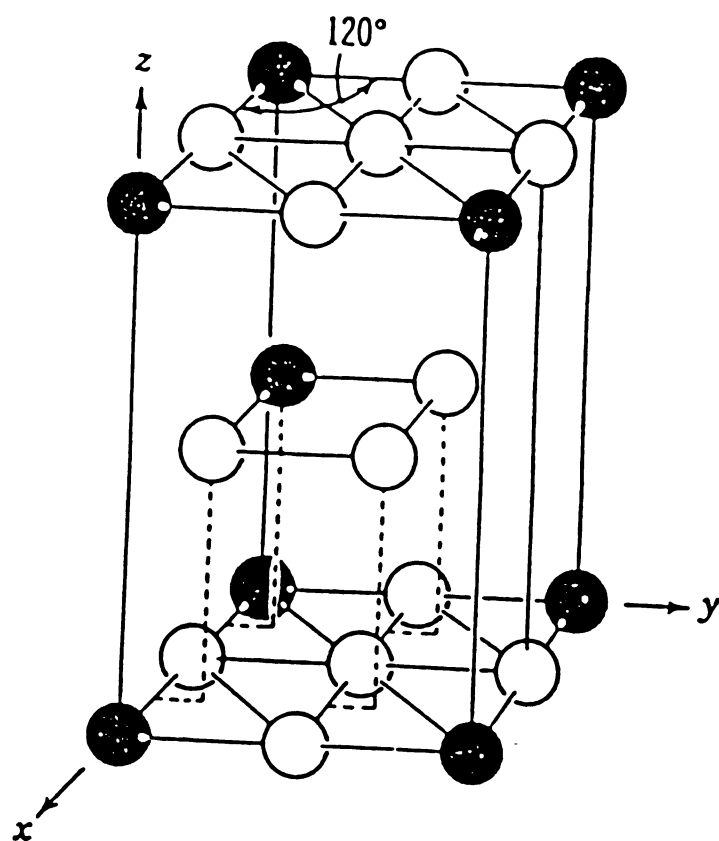


Figure 12. Provisional Ti-Al Phase Diagram (Titanium-rich end).

plays a prominent role is illustrated in fig (11) where the Ti-rich corner of the Ti-Al-Mo phase diagram at 700°C is revealed. It is recognised that these phase relationships are affected by the unintentional addition of interstitial impurity elements like oxygen, hydrogen, and nitrogen. R. D. Shull, et al [56] reported experimental data on the binary Ti-Al system which were useful in locating the $\alpha/\alpha+\alpha_2$ phase boundary in this system fig (12) by filling in the gaps in previously reported data. Conclusive evidence was provided for the detection of the $\alpha \rightleftharpoons \alpha_2$ order/disorder transformation using DSC (differential scanning calorimetry). Extreme precautions were taken to eliminate as much as possible hydrogen, oxygen, during the manufacture of Ti-6211 for experimentation. The range of aluminum compositions studied was between (10 at percent to 21 at percent). Selected area diffraction was used to confirm superlattice ordered spots. In the disordered hexagonal phase aluminum atoms are substituted randomly for titanium atoms, and in the ordered hexagonal (α_2 phase) of Ti_3Al -type (DO_{19} structure), there are definite positions for the aluminum atoms fig (13). The α_2 phase is coherent with parent lattice, the mismatch in lattice parameters being a few percent. Because of the lattice similarities, the electron diffraction patterns of the two phases differ only in the appearance of additional superlattice spots when α_2 is present. Fig (14) illustrates the DSC data with $H = 4.2 \text{ J/g}$ highlighting $\alpha_2 \rightleftharpoons \alpha$ order disorder transformation. R. D. Shull, et al. [56] also



The unit cell associated with the
DO₁₉-type superlattice.

Fig.13.

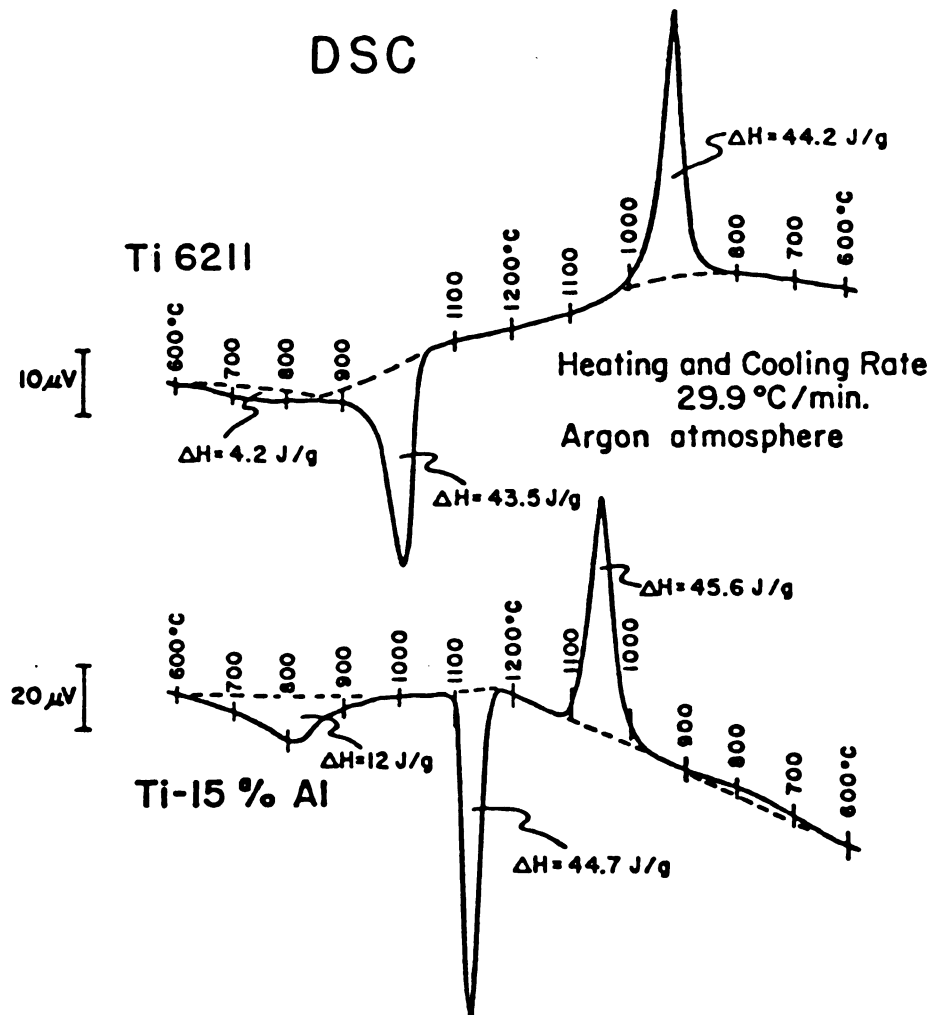


Fig.14. Differential scanning calorimetry data obtained on a Ti-15 at.% Al sample aged at 625°C for 378 hours and on an as-received sample of alloy Ti-6211.

conducted experiments on Ti-Al-Mo alloys containing a constant $\frac{1}{4}$ at. percent Mo and Al contents ranging from 10 to 21 at. percent. It was found that for these ternary Ti-Al-Mo alloys the same α_2 precipitates appeared as in the case of binary Ti-Al alloys. The size of the α_2 precipitates ranged from a few nanometers to several hundred nanometers; the higher the temperature and the closer the heat treatment to the phase boundary, the larger the precipitation size. The criterion for identifying equilibrium α_2 precipitates is the observation of distinct superlattice spots coupled with dark field images that show homogeneous distribution of α_2 . Fig (15) shows the results for the ternary alloy Ti-Al-Mo_{.25}. The filled circles indicate those samples where equilibrium α_2 was found as stated above, and the open circles indicate those samples where equilibrium α_2 was not observed. The thin background lines indicate the binary Ti-Al phase diagram (Fig 12). The thick solid lines indicate the $\alpha/\alpha+\alpha_2$ and $\alpha/\alpha+\beta$ boundaries determined for this system. It is suggested that the $\alpha/\alpha+\alpha_2$ boundary shifts towards higher Al contents on the addition of $\frac{1}{4}$ at. percent Mo. Specifically the presence of Mo shifts the $\alpha/\alpha+\alpha_2$ boundary toward higher Al contents and shifts the $\alpha/\alpha+\beta$ boundary toward lower temperatures.

Recently, we observed α_2 precipitates in Ti-6211 after an aging at 450°C for 72 hrs confirming the presence of ordering in this alloy. Details will be furnished in the results and discussion section of this thesis.

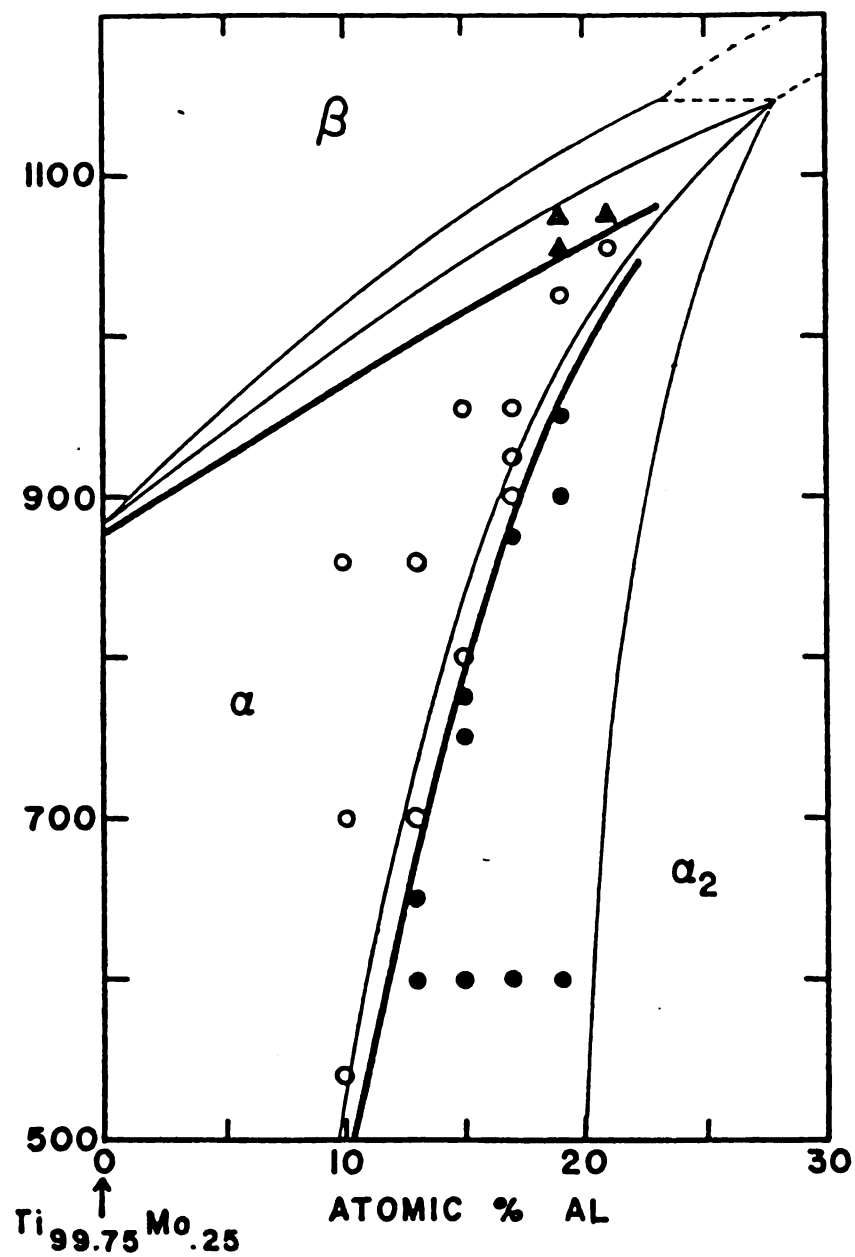


Fig.15. Ti-Al-Mo_{0.25} isopleth. Thin background lines indicate the diagram for the binary Ti-Al system. Data points from this study for the $\alpha+\alpha_2$ (●), α (○), $\alpha+\beta$ (▲) phase fields are also shown.

2.1.7 The Interface Phase

As early as 1966 the nature and structure of the interphase boundaries between the alpha and beta phases in $\alpha+\beta$ titanium alloys was recognised as complex, but no detailed analysis was attempted. Since then more information is available regarding the nature and crystallography of the interface phase which nevertheless is controversial. A profound interest in this region stems from the fact that the interface phase plays a significant role in various mechanical properties. The alpha/beta interfaces may influence the fracture behaviour of Ti alloys since they can provide crack paths for fatigue failures, and tensile overload failures. Strength and ductility may be affected if the presence of the interface phase inhibits the transfer of slip between the alpha and beta phases. Rhodes and Williams [57] have reported that in Ti-6Al-4V alloys the interfacial region is seen to be composed of a densely striated layer. It was at first suspected to be titanium hydride but this conclusion was not confirmed after further experimentation. Titanium hydride shrinks and disappears when heated to a temperature above the solvus which was not exhibited by the interface phase. Rhodes and Williams [57] summarised the fact that the interphase face that forms in alpha/beta boundaries is neither titanium hydride nor simply a region of high dislocation density, but it is a distinct layer which develops either as hexagonal-alpha phase having a different orientation than the primary alpha into which it grows, or as

an fcc phase depending upon heat treatment. The occurrence of the complex interphase boundary appears generally in all titanium alloys containing alpha/beta boundaries which have formed at temperatures in the range 675 to 875°C. Margolin et al. [58] have postulated that the interface phase is related to the precipitation of alpha, and that the thickness of the interface structure is approximately the same as the thickness of Widmanstätten alpha and the alpha projections which emanate from the coarse Widmanstätten alpha. Formation of the interface phase generally appears to take place when precipitation of alpha would be expected to occur. Precipitation of alpha from beta involves volume expansion since alpha has a lower density than beta [59], the difference in size must be accommodated by both phases and hence volumetric strains have to be considered in the formation of the interface phase, and may contribute to the formation of the fcc phase noted by Rhodes and Williams. The presence of a fcc structure, twinned alpha or a heavily dislocated layer of alpha of different orientation than the contiguous alpha suggests that these interface structures need not produce embrittlement of alpha-beta alloys [58] several observations support this point of view. Slip lines have been observed to pass readily across this interface from alpha to beta under both tensile and fatigue loading conditions, a process which suggests that the interface structure, presumably present, is not a significant barrier. It was suggested by Margolin et al. [58] that the interface

phase may contribute to void formation by promoting incompatibility between alpha and beta. But by itself this assumed enhancement in void formation potential would not necessarily lead to decreased ductility, and the largest degree of incompatibility would be promoted at interfaces of equiaxed alpha and beta [58]. Rhodes and Paton [60] studied the conditions for formation of the interface phase in Ti-6Al-4V. Their previous work had indicated that the interfacial layer could form either with an fcc structure or with an hcp structure, and evidence was presented that the interface phase was alpha phase in a "non-Burgers" orientation or in a Burgers orientation different from that of the adjacent primary alpha. They also concluded [60] that the interface phase does not grow during isothermal treatments, but rather grows only during cooling from elevated temperatures to about 650°C. The width of the interfacial layer is a function of the cooling rate, having a maximum of about 4000 Å at 28° C/h. The interface phase forms initially with an fcc structure which subsequently transforms to hcp alpha phase. The layer has been shown previously to occur either with a dense internal structure (called striated alyer) or with no internal structure (called a monolithic layer). The striated layer was interpreted as having the hcp structure of the alpha phase, but in a different orientation from the adjacent primary alpha. The monolithic layer was shown to have an fcc structure [60] and obeys the crystallographic relationship

$$(110)_{\beta} // (111)_{\text{fcc}} // (0002)_{\alpha}$$

and $[111]_{\beta} // [110]_{\text{fcc}} // [11\bar{2}0]_{\alpha}$

It was suggested that the fcc monolithic layer phase may be a transition structure in the β - α transformation [60], and also that the interface phase may result from sluggish beta stabiliser (vanadium) diffusion away from the transforming (beta — alpha) interface region. Williams studied the occurrence of interface phase in Titanium-6211, and fig (16) reflects a concentration profile of solute in four regions of beta, fcc interface phase, hcp interface phase, and alpha phase. The conc. range of each phase is illustrated by two dashed lines. Darkened lines α_1 and α_2 define the concentration range of both hcp interface phase and alpha phase. Since they have the same crystal structure, the concentration discontinuity is not expected to exist between them, but this suggestion by Williams is prone to speculation because concentration difference could exist as a consequence of elastic misfit energy which can give rise to difference in chemical potential in two regions of a single phase. This concentration profile according to Williams can be applied to specimens which were beta solution treated and cooled to a temperature below 840°C (where the fcc interface is stable). It can also be applied to beta worked material (as received) which has been $\alpha+\beta$ solution treated at temperatures where fcc interface phase is stable, eg: 700°C. Williams showed that in Ti-6211 the alpha/beta interface structure consists of two different layers of interface phase, a monolithic layer (fcc structure) and a hcp layer with dense

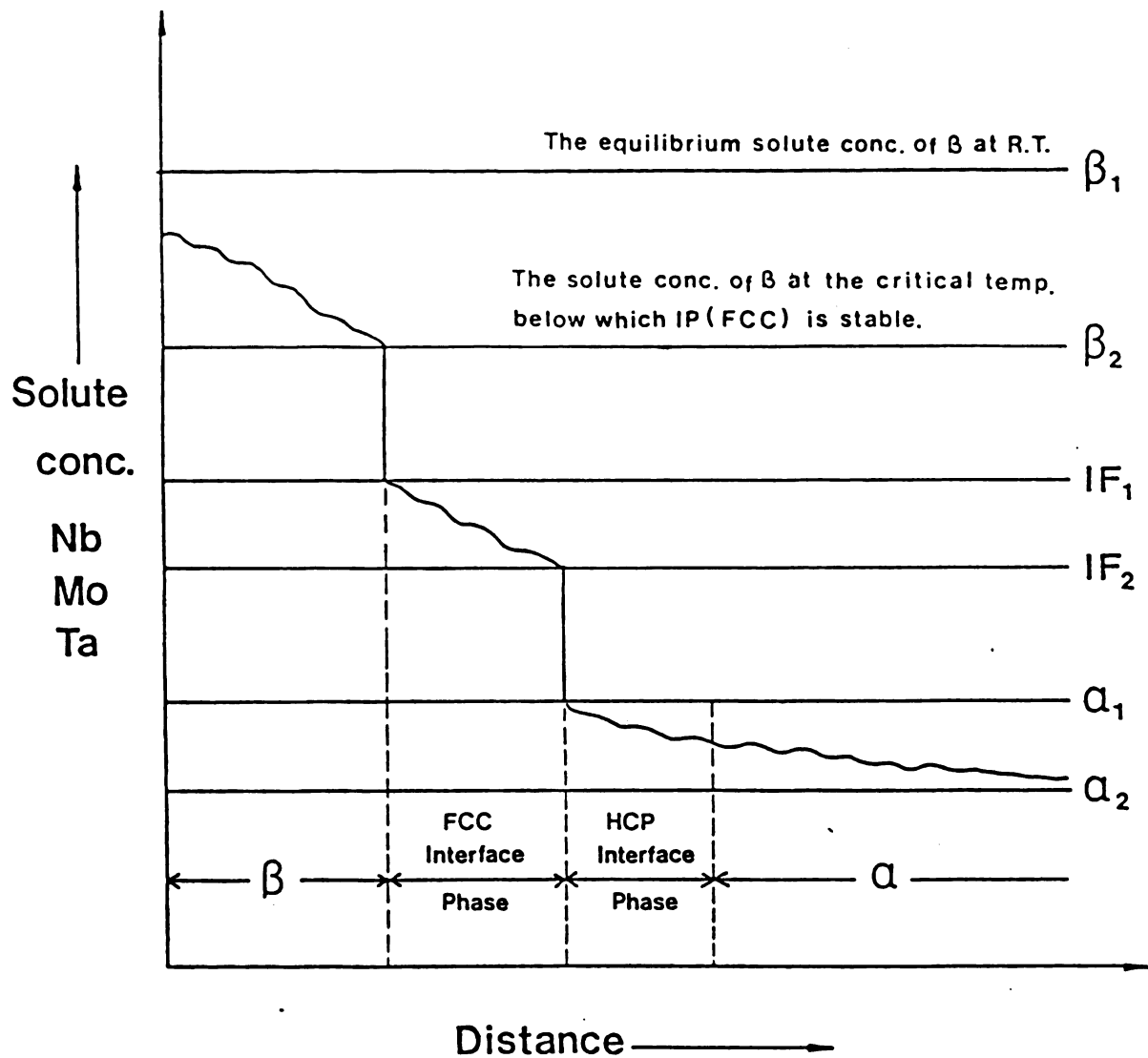


Fig.16. The schematic description of solute concentration profiles in four regions consisting of β , fcc interface phase, hcp interface phase, and α phase.

internal structure. The fcc interface is unstable at 840°C and above, and the critical temperature below which fcc interface phase is stable is believed to be between 820°C and 840°C . The concentration of beta stabiliser elements (Nb, Mo, Ta) in beta, fcc interface phase (IF), hcp interface phase (IH), and alpha vary in the following order:

$$\beta > \text{IF} > \text{IH} > \alpha$$

According to Williams the most often observed orientation relationship of alpha, fcc interface phase, and beta phase is as follows

$$(0002)_{\alpha} // (\bar{1}00)_{\text{fcc}} // (0\bar{1}1)_{\beta}$$

$$[11\bar{2}0]_{\alpha} // [011]_{\text{fcc}} // [111]_{\beta}$$

Banerjee and Arunachalam [61] studied the interface phase in titanium alloys like BT₉ and IMI 685 and found the interface phase to be thermally unstable at 873 K, and the time taken for complete dissolution of the phase as suggested by them is 64 hours at this temperature in BT₉. The Rhodes Paton model [60] for the formation of the fcc phase has been shown to be inapplicable in these alloys, and that the fcc interface phase is titanium hydride. Banerjee and Arunachalam [61] visualised the formation of titanium hydride as follows: As the beta — alpha transformation proceeds on cooling the alloys through the transus, partitioning of various alloying elements occur. The partitioning of hydrogen must be particularly strong below 573 K where the solubility of hydrogen in alpha decreases rapidly. Hydrogen atoms migrating from the alpha phase to the interface phase will

precipitate in this region since the supersaturation exceeds the solubility limit. The precipitation event takes place when the beta — alpha transformation is complete. Recently Banerjee, Williams et al. [62] have suggested that the interface phase (face centred cubic or hexagonal structure) is an artifact produced by the electrolytic technique used in thin foil preparation. Results were based on a near alpha alloy Ti-6Al-1.5Zr-3Mo-0.25Si and Ti-10V-2Fe-3Al (metastable beta alloy). Foils from these samples were prepared by jet polishing in a solution containing 6% H_2SO_4 in methanol at 223 K in a Fischione jet polisher or by ion milling from the bulk. Different starting thickness of 0.05 mm and 0.1 mm were employed for electropolishing in order to study the effect of sample thickness and electropolishing time on interface phase formation. Results suggest that the face centered and the hexagonal interface phases in titanium alloys arise out of processes occurring during the electrolytic preparation in thin foils [62]. The authors believe that the fcc phase is formed in alloys containing low volume fractions of beta and where the starting thickness of the discs used for electrothinning is high (polishing times are longer). The fcc phase was confirmed to be a hydride of titanium, which forms as a result of an increase in hydrogen concentration in the thin foils during electropolishing. Westlake and Gray have shown the hydrogen content in materials such as V, Ta, Nb can increase as much as four times during electropolishing [63], depending on the starting

thickness. The hexagonal interface phase occurs when the amount of fcc phase formed is low and when the starting thicknesses are low and/or the beta volume fraction is high. It is suggested that the hexagonal interface forms due to stresses at the alpha/beta interface arising from the thin foil relaxation in the beta phase during electropolishing.

3. REVIEW OF RELEVANT ELECTRON-ANALYTICAL TECHNIQUES

Three relatively new techniques were used in phase identification and solute partitioning in Titanium-6211.

1. Scanning transmission electron microscopy (STEM)
2. Microdiffraction in STEM
3. Microchemical analysis in STEM

Following is a brief review of the above mentioned techniques.

3.1 Scanning Transmission Electron Microscopy

STEM served as a very important technique in the phase identification and characterisation of the titanium alloy in this project. The microscope utilised was a vacuum generator model 5 installed scanning transmission electron microscope. An understanding of the working, and capabilities of this microscope is worth highlighting as part of this project.

In STEM an electron transparent specimen is illuminated by a small scanning electron beam, similar to that in the scanning electron beam microscope (SEM) rather than by a relatively large diameter stationary beam as in conventional transmission electron microscopy. STEM has all the capabilities of TEM to define microstructure quantitatively as well as to perform simultaneously chemical analysis of areas of the specimen on a tenth nanometer scale. Polymers that get degraded under the electron beam in TEM can be investigated readily in STEM for longer times. SEM techniques such as imaging with secondary and primary back

scattered electrons, production of channeling patterns etc, can be done with STEM techniques; Fig (17) illustrates the STEM set up. Incident beam is scanned over the specimen, and the STEM image formation is detected for one image point at a time. The detector is normally a phosphor-photomultiplier combination which provides an electrical image signal in serial form for display on a cathode ray tube after recording in an analog or digital form. To achieve good quality imaging, a good signal to noise ratio is required which means that the number of electrons scattered from each picture element within a short period must be around 10^4 or more. To attain high resolution imaging this number of electrons must be concentrated within a very small probe size. This demands a high intensity electron source from the use of a field emission gun.

3.1.1 Microdiffraction in STEM

An important feature of transmission electron microscopy is the capability of obtaining both a high resolution electron micrograph and an electron diffraction pattern from the same selected area of the specimen. Consequently considerable effort has been made to reduce the size of the area from which the diffraction pattern is obtained. In today's modern conventional transmission electron microscope (CTEM), the standard selective area diffraction technique (SAD) allows area selection of approximately $2000\text{\AA}$ diameter minimum. With the introduction of STEM, important new techniques have been developed which extend the capability

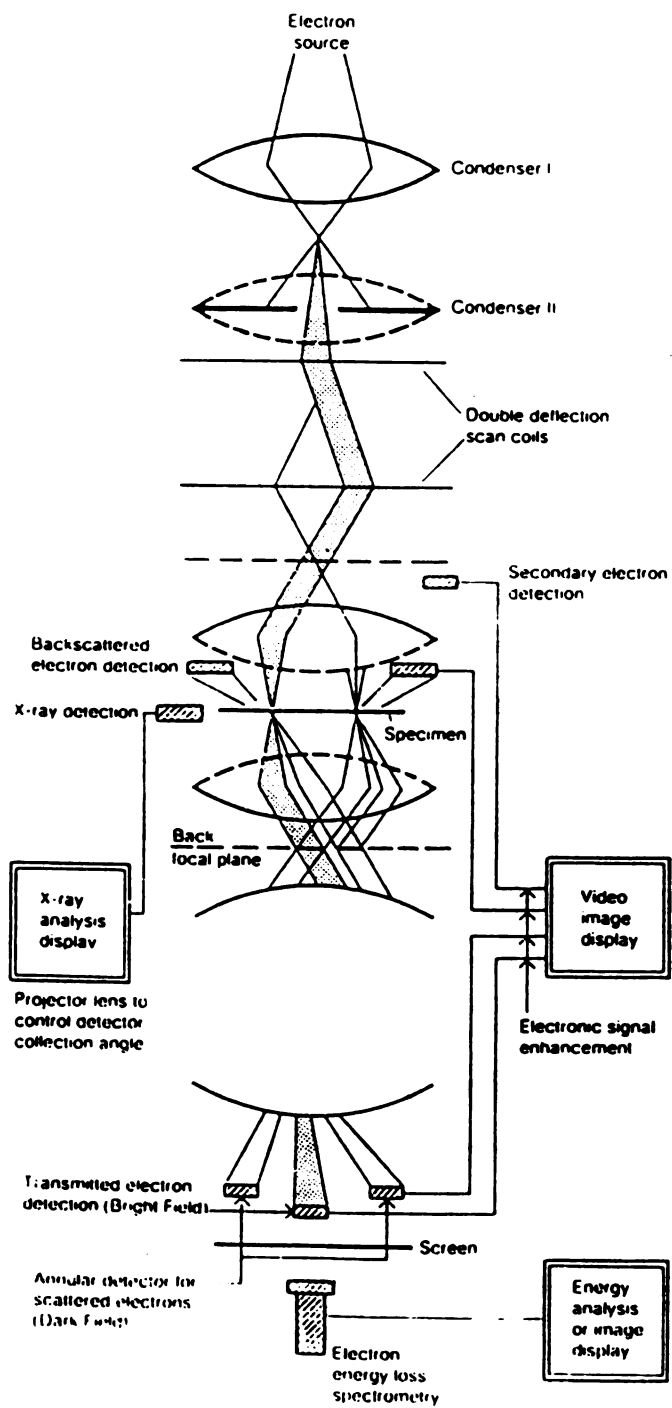


Fig. 17.

of SAD to less than $30 \text{ \AA}^\circ$. Using the criteria that the minimum crystal size for a meaningful diffraction pattern should be 5 times the unit cell size, the goal of minimum area electron micro-diffraction has essentially been achieved. The procedure used to obtain microdiffraction patterns depend in part on the electron optical configuration of the objective lens in the electron microscope. The most straight forward technique uses the convergent beam diffraction pattern (CBDP) obtained with the electron probe formed for STEM imaging. Stopping the probe on the area of interest forms a CBDP in the back focal plane of the objective lens which may either be recorded on photographic film directly or displayed on a CRT by means of Grigson coils placed beneath the objective lens. The resolution of the pattern is determined by the angular aperture of the convergent beam probe which is typically about 10 mrad. Defocussing the probe allows the angular resolution of diffraction patterns to be improved to one mrad or better from areas about $200 \text{ \AA}^\circ$ in diameter. In another method the specimen is positioned approximately midway between the objective lens pole pieces such that a near parallel incident beam may be rocked about a point lying on the specimen plane. A sequence of dark field intensity maxima are formed at the detector and subsequently displayed on the CRT. Diffraction patterns from areas less than $30 \text{ \AA}^\circ$ in diameter have been obtained with an angular resolution of 3 mrad using this technique. These techniques provide single crystal spot

patterns from which phase identification and/or orientation may usually be determined. An alternative approach employs dynamical diffraction in CBDP to obtain more accurate data from larger areas ($100\text{-}500\text{ \AA}^2$) orienting the specimen on zone axes where dynamical diffraction occurs.

A comparison of techniques shows that both the fixed probe CBDP method and the beam rocking method yield diffraction patterns from extremely small areas; however, specimen contamination in existing commercial instruments may be a serious problem in the case of the CBDP method, suggesting that beam rocking may be more appropriate when studying regions of less than $100\text{ \AA}$ diameter. Neither the fixed probe CBDP method nor the rocking beam technique seem to have deleterious effects on metallurgical specimens with regard to beam heating or radiation damage at accelerating voltages up to 100 KEV. However an intense beam of electrons is required to obtain information from such small areas, hence there may be damage in many of the non metallic beam sensitive materials. Other methods of electron diffraction are the use of optical means to obtain selected area diffraction patterns and high dispersion or small angle electron diffraction.

3.1.2 Electron Beam Microanalysis in STEM

Electron beam microanalysis is a powerful analytical technique capable of performing elemental analysis of microvolumes, typically on the order of a few cubic microns in thick samples and considerably less in thin sections.

Analysis of X-rays emitted from a sample can be accomplished by energy dispersive spectrometers which permit analysis by discriminating among X-ray energies or by crystal spectrometers which use a diffracting crystal to select the wavelength of interest. The former method is called energy dispersive spectroscopy (EDS) and the latter wavelength dispersive spectroscopy (WDS), is an older method. EDS and WDS can analyse elements beginning with sodium in the periodic table. It is possible to detect less than 10^{-16} grams of an element present in a specific microvolume of a sample. The development of the EDS system has been strongly linked to advances in computer technology. Electron energy loss, and wavelength dispersive spectrometers are routinely interfaced to the EDS computer for data collection, storage and processing.

3.1.3 Principles of EDS system operation

The backbone of the EDS system is a silicon diode typically 12.5 mm^2 in active area and 3 mm in thickness. If the diode is reverse biased by approximately 1000 volts a depletion region is established. All of the normally present electrons and holes in the depletion region are removed (by the external field). If an X-ray photon is absorbed within the depletion region, producing a number of electron-hole pairs these charge carriers will be swept out by the electrical field and they will appear as a pulse of charge on opposite sides of the diode. This charge is converted into a voltage pulse, amplified and shaped, its amplitude is

converted into a digital signal and the resulting information is analysed.

The total time the system is not available to accept pulses (during the processing of a pulse or while the system is gated off due to pile up rejection) is called "dead time". Since pulses may have been arriving while the ADC was busy, the time of the analysis is extended by the live-time corrector to compensate for this dead time. Live time correction is necessary to measure the true count rate for a given element, a parameter required for quantitative analysis and for accurate comparison of two spectra accumulated at different count rates. Because the electronics of the EDS system must have both sort and count X-ray events, the total count rates that can be processed are much lower than those of a WDS system (where the sorting is done by crystal diffraction). The resolution of a given ED spectrometer is defined as the full width at half maximum height (FWHM) of the peak above background at 5.9 KeV (Mn K_{α}). The resolution is determined by statistics of charge production, detector and preamplifier noise, and degree of incomplete charge collection.

3.1.4 Qualitative EDS microanalysis

Perfect qualitative analysis would permit identification of all elements present in any selected region of the sample imaged on the microscope. Limitations on the ability to perform such an analysis arise from considerations of detectability limits, spatial resolution, and spectral resolution.

The minimum detectable quantity of a given element, or

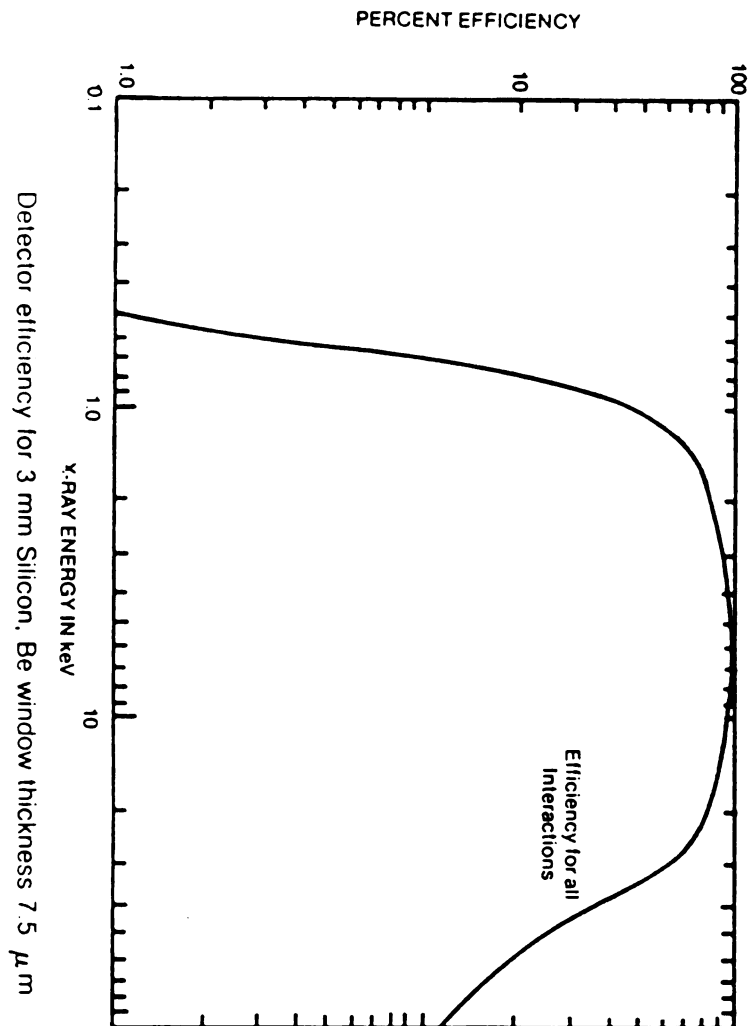


Fig. 18.

its detectability limit varies with many factors like the X-ray line used for analysis, accelerating voltage, matrix, detector efficiency, sample geometry, peak counting time, and peak and background counting rates. Elements below fluorine in atomic number are generally not detectable at all.

The silicon diode spectrometer is nearly 100 % efficient over a wide portion of the analytical range. At low energies, however, the efficiency goes down because of absorption of X-rays in the beryllium window and other detector surfaces. At higher energies the spectrometer again becomes less efficient due to the ability of these X-rays to pass completely through the detector. Fig.(18) illustrates this.

Spatial resolution plays a very important role in microanalysis and data collection by the EDS. The goal in electron beam microanalysis is to analyse small volumes of a sample that correspond to a particular structural feature in the electron image. Resolution of $100 \text{ \AA}$ is possible with thin sample sections and small intense probes. The main consideration in the weakening X-ray spatial resolution is the spread of the electron beam as it penetrates the material. Secondary electrons which form the image are very low energy, coming from only a thin surface layer on the order of $100 \text{ \AA}$ in depth, where the beam has not spread significantly in the lateral direction. Secondaries continue to be generated as the electron beam penetrates the sample, but do not escape and do not contribute to the image. High energy back scattered electrons can escape from much greater depths in the sample, thus a back scattered image is of poorer resolution than the secondary

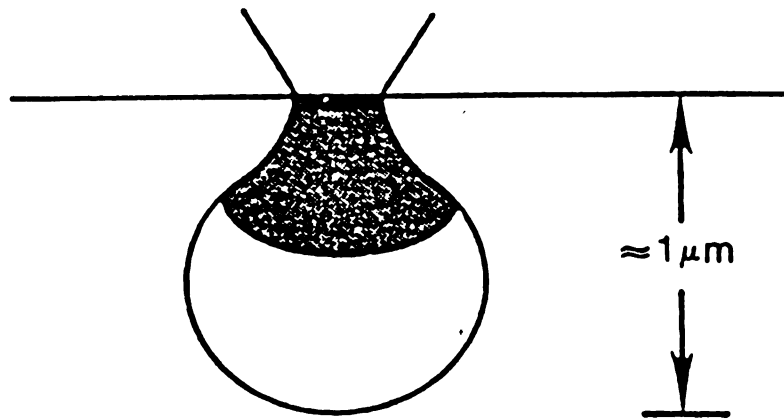


Fig.19. Escape depth for secondary electron, backscattered electron emission and X-ray

image. Finally, X-ray can contribute to be generated by the primary beam and being able to travel further in matter than electrons, escape from still larger depths in the sample. Fig.(19) illustrates this fact. It is clear that one can see features in the secondary electron image that can not be uniquely analysed in the X-ray analysis. For example a surface particle $1\text{ }\mu\text{m}$ in diameter but only $100\text{ }\text{\AA}$ thick, may be readily visible in the image, however, most of the X-ray information comes from a region below the particle and the analysis obtained will not be specific to the imaged particle. Hence one must be aware of this fact to interpret microanalysis results. One technique to improve X-ray spatial resolution is to decrease the accelerating voltage thereby decreasing penetration of the electron beam in the sample. By using thin sections the electron beam is not given the opportunity to spread very far in the lateral direction. In this case the resolution continues to be improved by reducing the probe size.

Spectral resolution is important in qualitative analysis because the X-ray lines of one element may be hidden under the lines of another causing the analyst to miss the identification of the overlapped peaks. In EDS peak overlap situations like the Mo L and S K lines can only be rectified by use of a crystal spectrometer.

Interpretation of SEM, TEM, X-ray diffraction techniques for this project will be discussed in the results and discussion section.

4. EXPERIMENTAL PROCEDURE

4.1 Heat Treatment

Ti-6211 plate (as received) was cut into smaller blocks of 2 cm by 1 cm in size using an abrasive cut off wheel. Samples were then polished to remove sharp projections and then encapsulated in a quartz tube at a vacuum of 10^{-5} torr. Solution treatment was done at 1050°C and then all the samples were step quenched at progressively lower temperatures of isothermal holding followed by quenching to room temperature. One particular sample was step quenched to 450°C and held for 72 hours to study the ordered α_2 phase formation. Heat treatment schedule adopted is illustrated in fig (20).

4.2 Study of Heat Treated Samples

4.2.1 X-ray Diffraction

Heat treated samples were cut to fit into the specimen holder of the X-ray diffraction unit. Sample surfaces were polished and lightly etched before subjecting it to diffraction. A philips Norelco X-ray diffractometer fitted with a LiF crystal Monochrometer was used with $\text{Cu K}\alpha$ radiation.

4.2.2 Scanning Electron Microscopy

Heat treated samples were polished on 240, 320, 400 and 600 emery papers, followed by disc polishing using 0.05 micron alumina. Samples were then etched for 60 seconds with

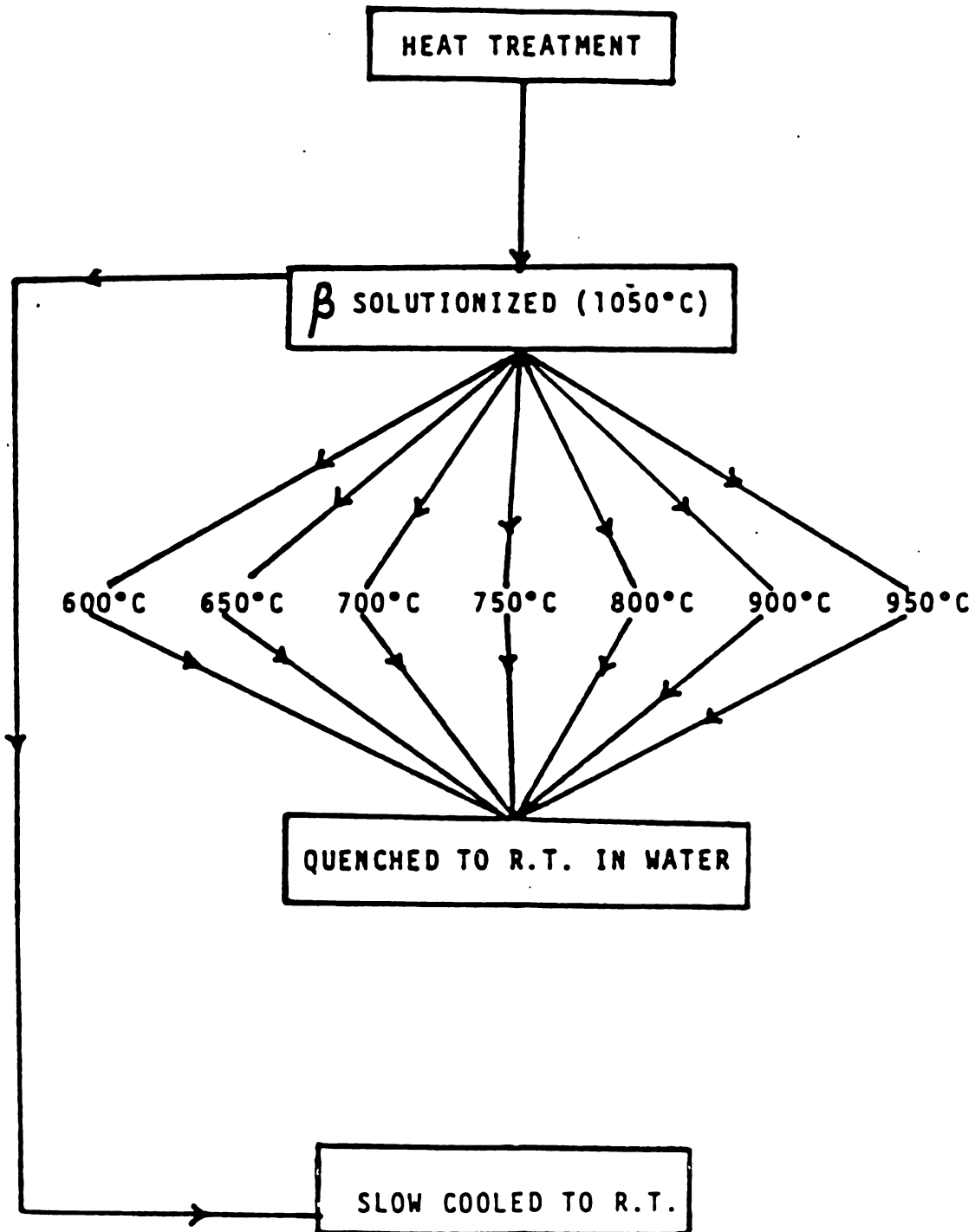


Fig.20. Heat treatment schedule

Kroll's reagent comprising of 95 cc H_2O , 3.5 cc HNO_3 , and 1.5 cc HF and then washed with water and methanol. A Hitachi 5-415A scanning Electron Microscope was used for this study.

4.2.3 Sample Preparation for TEM/STEM

The preparation of samples for TEM and STEM studies were identical, comprising of the following steps.

- 1) Specimen slicing to about 0.5 mm by diamond wafering blade.
- 2) Hand grinding on coarse emery paper to a starting thickness of about 150 μm .
- 3) Shaping the samples to 3 mm diameter and 150 mm thickness
- 4) Jet polishing to achieve a dish on either side of the sample using the following chemicals and conditions.

30 ml perchloric acid

175 mls butoxyethanol

295 mls ethanol

voltage 120; current 130-140 mA

- 5) Final polishing to achieve a small hole at the center of the specimen.

6 ml perchloric acid

175 ml butoxyethanol

295 ml ethanol

voltage 12-50 volts, current 20mA, Temp $-45^{\circ}C$
to $-55^{\circ}C$

5. RESULTS AND DISCUSSION

5.1 X-ray diffraction studies

All the heat treated samples, representing various isothermal holding temperatures, were subjected to X-ray diffraction. Figs (21) and (22) illustrate the critical bragg angles at which the phases are identified. Between the 20 values of 33° to 43° and 72° to 80° identifiable primary or untransformed beta phase and the orthorhombic martensite phase have been detected. The $(202)_{\alpha''}$ martensitic peak shows a decrease in intensity for holding temperatures from 650°C to 900°C , and decreases in intensity for holding temperatures greater than 900°C . This suggests the fact that there is a critical temperature range in which orthorhombic martensite is formed. This result however is affected by a strong texture and grain growth. There is also a shift of $(110)_{\beta}$ peak to higher angles with decreasing heat treatment temperatures. This suggests that there is a contraction in lattice parameter of the retained beta phase with decreasing temperature. Molybdenum is the only element in Ti-6211 which decreases the lattice parameter of the beta phase and hence it is suggested that supersaturation of the beta phase with Mo occurs at lower annealing temperatures. This could lead to a critical beta phase lattice parameter at which $\beta\text{-}\alpha''$ transformation occurs. From the model proposed by Mukherjee Kato [27] and from X-ray diffraction experiments lattice

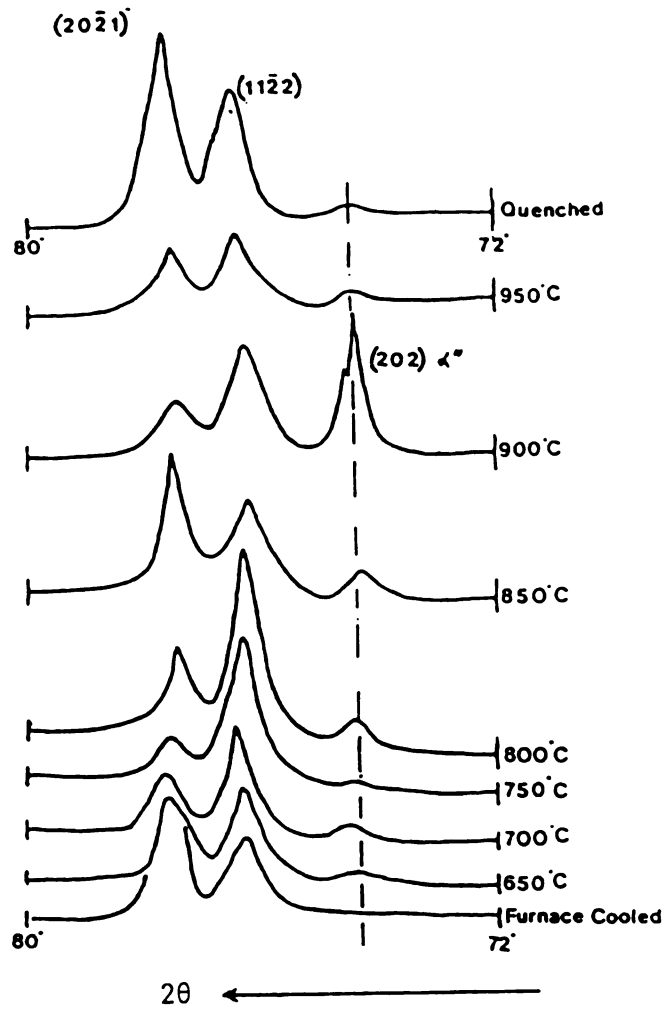


Fig.21. Composite X-ray peaks; CuK_α radiation

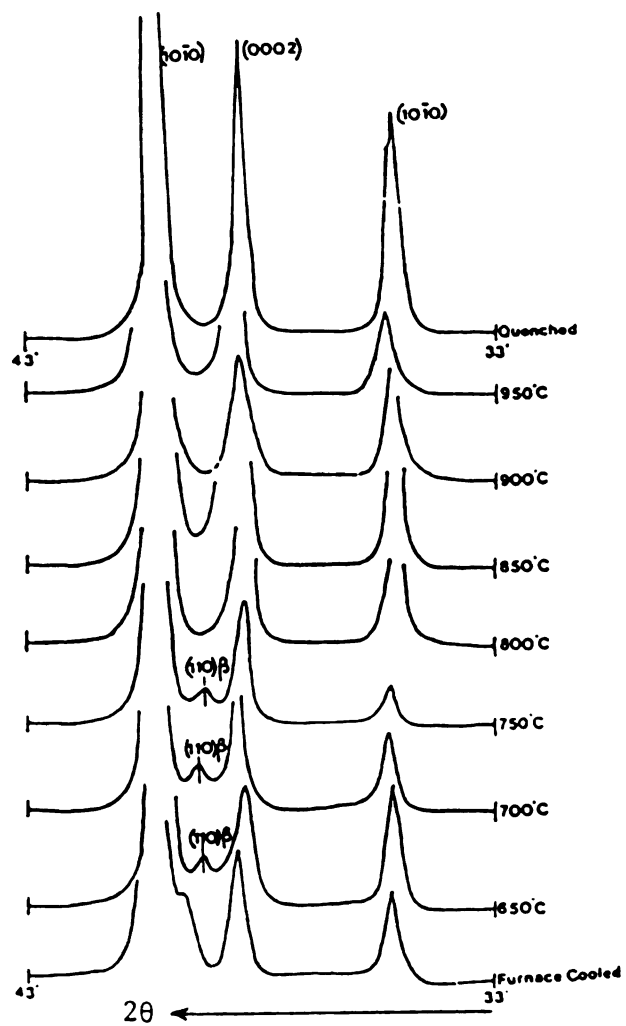


Fig.22. Composite X-ray peaks; $\text{CuK}\alpha$ radiation.

parameter of the orthorhombic martensite phase was calculated as $a = 3.04 \text{ \AA}$, $b = 4.94 \text{ \AA}$, $c = 4.64 \text{ \AA}$.

The lattice parameter of the beta phase at room temperature was also calculated to be $a = 3.23 \text{ \AA}$. Since the M_s temperature for the α'' -martensite is higher than room temperature, the actual lattice parameter of the beta phase at the M_s temperature is greater than $3.23 \text{ \AA}$ due to thermal expansion as well as due to lower Mo content of the beta phase at higher temperature. However, in the first approximation, these lattice parameter values can be used to compute the habit plane of the α'' martensite by using the model suggested by Mukherjee and Kato 27 . The calculated habit plane from such a calculation is: (239).

5.2 Transmission Electron Microscopy

TEM studies were conducted to investigate the phases present at various isothermal holding temperatures. Before discussing the results obtained it would be appropriate to refer to the schematic beta isomorphous diagram of Ti-6211 as suggested by Williams Fig (23). As the isothermal holding temperature decreases the volume percent of beta decreases (lever rule), and the alloying element content in the beta phase increases rapidly. The alloying element in the alpha phase increases slightly with decrease in isothermal holding temperature. Thus depending on the solution heating temperature, the beta phase in Ti-6211 alloy can undergo transformation to α' or α'' martensites or can be retained in a metastable condition upon quenching from elevated

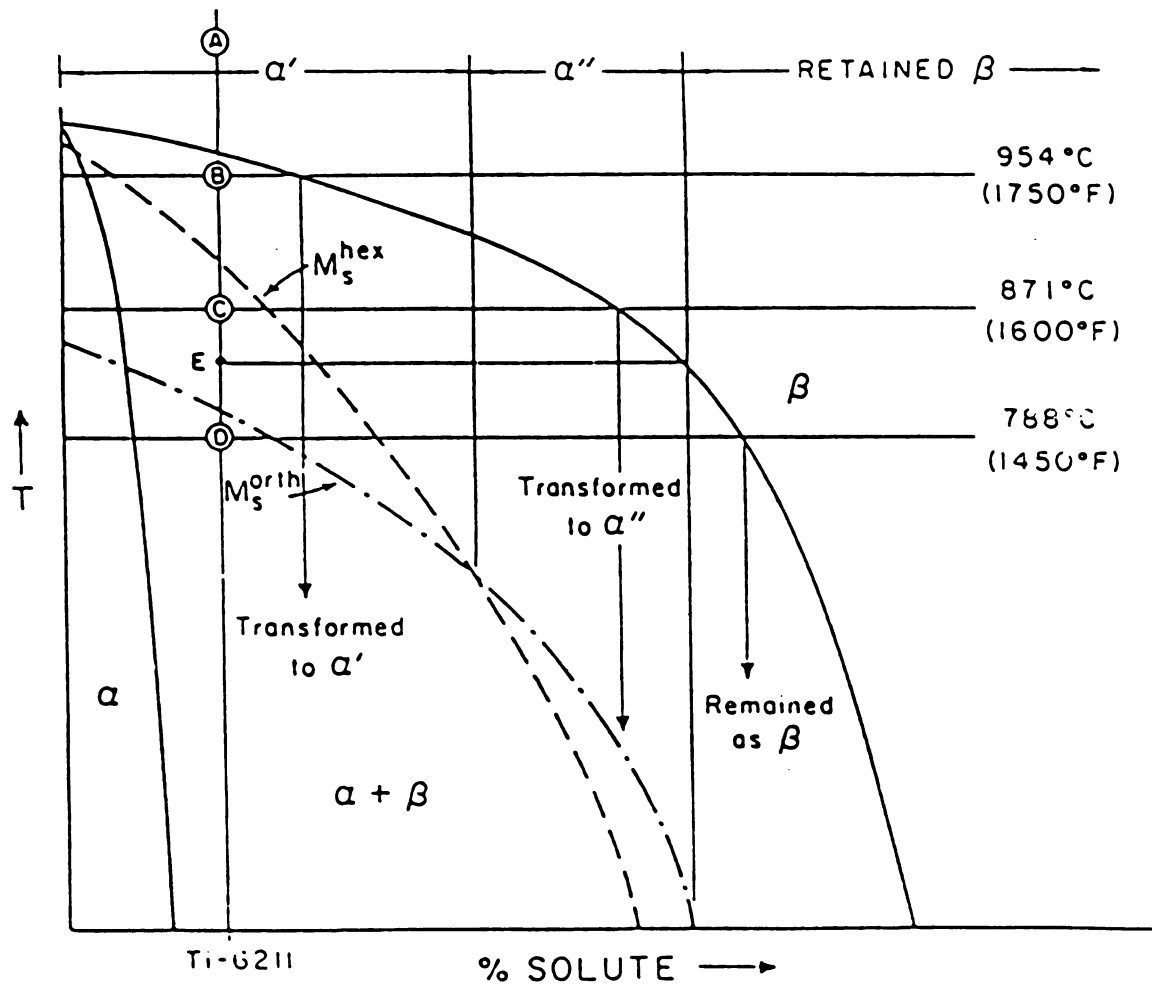
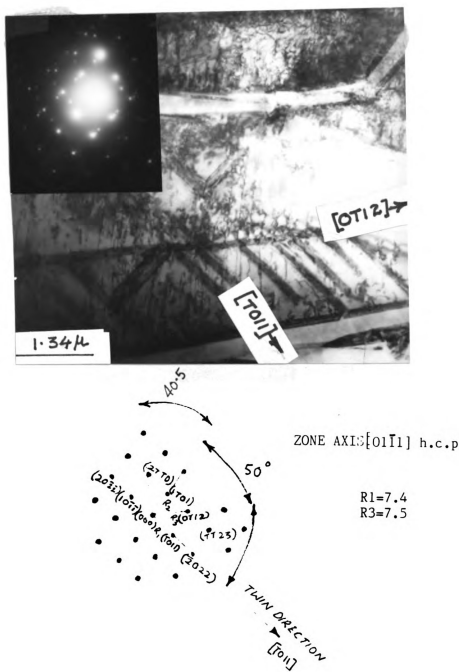


Fig.23. The schematic phase diagram of Ti 6211

temperatures. At high $\alpha+\beta$ solution treatment temperatures, beta transforms to α' , at the intermediate temperature range beta transformed to α'' and at low temperature range the beta phase is retained. The transformation products depend on solute concentration of the beta phase.

TEM studies for 950°C isothermal holding temperature reveal twinned hexagonal martensite formation Fig (24) and the associated selective area diffraction patterns confirm the hexagonal crystal structure. Bright fields for 850°C isothermal holding temperature show alpha platelets with the interface phase exhibiting high dislocation density fig (25) unlike the 950°C specimen which does not reveal any predominant interface phase region. The alpha platelets are of the Widmanstatten type with dislocation lines running across them. Examination of 750°C TEM specimens reveal a more pronounced Widmanstatten morphology of alpha platelets with dislocation fields surrounding the interface fig (26), suggesting the fact that the interface region is stressed as a result of alpha transformation from parent beta phase. Specimens held at 700°C isothermal holding temperature show beta platelets fig (27) as confirmed by SAD patterns. TEM results show that as one goes to lower isothermal holding temperature the tendency for beta to remain untransformed is more, and the interface phase ceases to form for temperatures below 750°C. The temperature range of 750°C-850°C allows the interface phase to be more stable. According to Williams the interface phase in the alloy is stable between 800° and



950° C SAMPLE

Fig.24 Bright Field and associated selected area diffraction

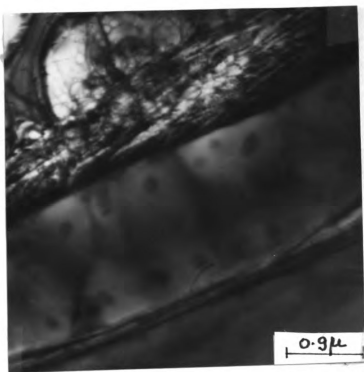
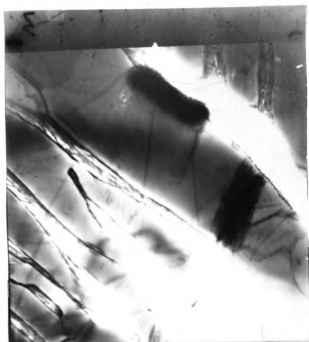
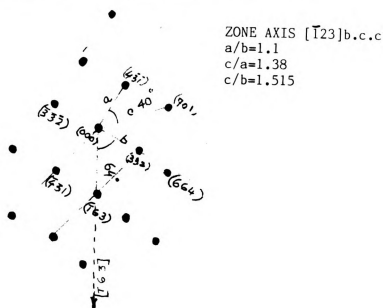


Fig.25. TEM sample isothermally held at 850°C showing dense dislocations at the interface

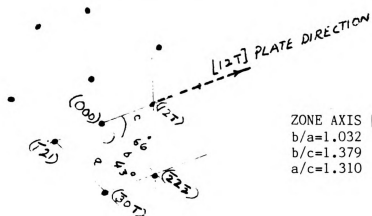
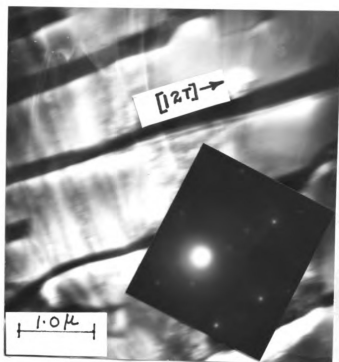


TEM sample isothermally held at 750°C for one hour showing alpha plates.



750°C SAMPLE

Fig.26 Bright Field and associated selected area diffraction showing alpha plates at the interface



ZONE AXIS $[123]$ b.c.c
 $b/a=1.032$
 $b/c=1.379$
 $a/c=1.310$

700° C SAMPLE

Fig.27

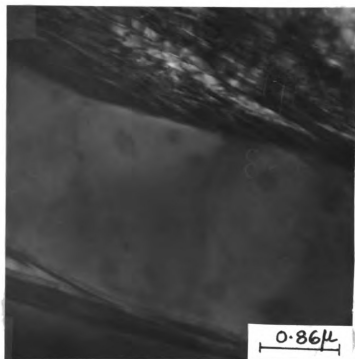


Fig.28. TEM micrograph of sample held at 850°C for one hour showing dense striations at the interface.

850°C. Dense internal structure fig (28) at the interface region suggests an hcp structure as per Williams. However since the appearance of the interface phase is very sensitive to contrast conditions, no authoritative comment can be made in this regard.

5.2 Scanning Electron Microscopy

Various isothermally held specimens were observed under scanning electron microscope. All the SEM micrographs reveal beta network interspaced with alpha. The amount of beta phase or titanium martensite decreases with decreasing temperature as seen in the SEM micrographs. In the case of the annealed sample, the $\alpha+\beta$ network is more widely spaced owing to the long duration of anneal permitting diffusion of atoms to longer ranges. The ordered structure α_2 could not be resolved in SEM owing to its limitation in magnification.

Isothermal annealing at 850°C reflects a higher percentage of beta transformed product as compared to temperatures below it. Figures 29-35 illustrate details Fig 35 reveals voids present in the alloy. The acicular morphology of martensite is clearly revealed with twins running across.

5.3 Scanning Transmission Electron Microscopy

The primary intention of using the technique of STEM was to study solute partitioning tendencies in this alloy at various temperatures. Microdiffraction was also done especially for determining the ordered phase α_2 . Appropriate bright field pictures were taken to illustrate the morphology

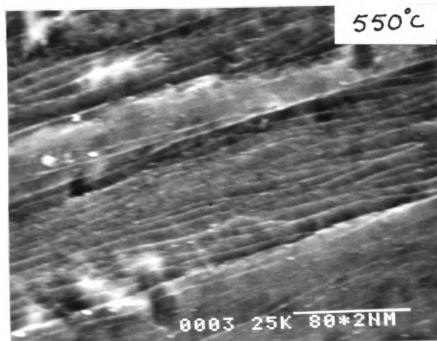


Fig.29. SEM micrograph of sample isothermally held at 550°C for one hour showing beta stringers interspaced with alpha

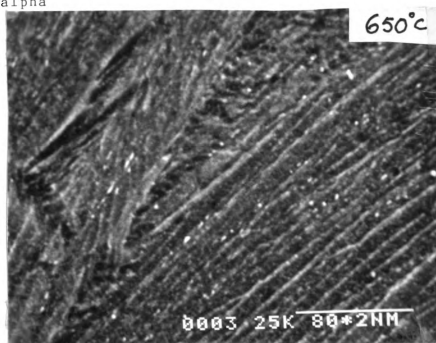


Fig.30. SEM micrograph of sample isothermally held at 650°C for one hour showing beta network interspaced with alpha.

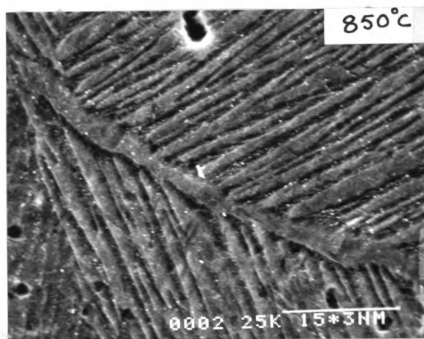


Fig.31. SEM micrograph of sample isothermally held at 850°C for one hour showing alpha at grain boundaries.

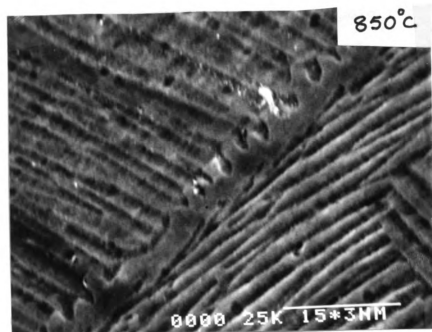


Fig.32

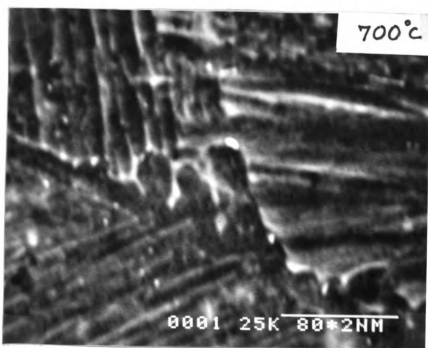


Fig.33. SEM micrograph of sample isothermally held at 700°C for one hour showing beta network interspaced with alpha.

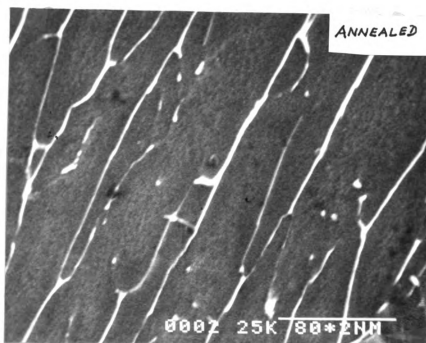


Fig.34. SEM micrograph of annealed sample held isothermally at 450°C for 72 hours showing beta stringers interspaced with alpha.

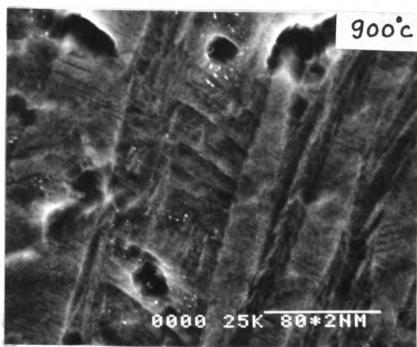


Fig.35. SEM micrograph of sample held isothermally at 900°C for one hour showing voids and acicular martensite.

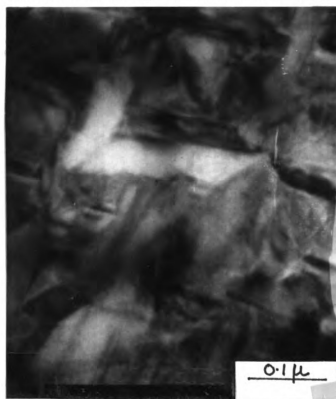


Fig.36. STEM micrograph of sample held at 750°C for one hour showing butterfly martensite.



Fig.37. STEM micrograph of sample isothermally held at 750°C for one hour showing acicular martensite.



Fig.38. STEM micrograph of sample held isothermally at 750°C for one hour showing twins in martensite.

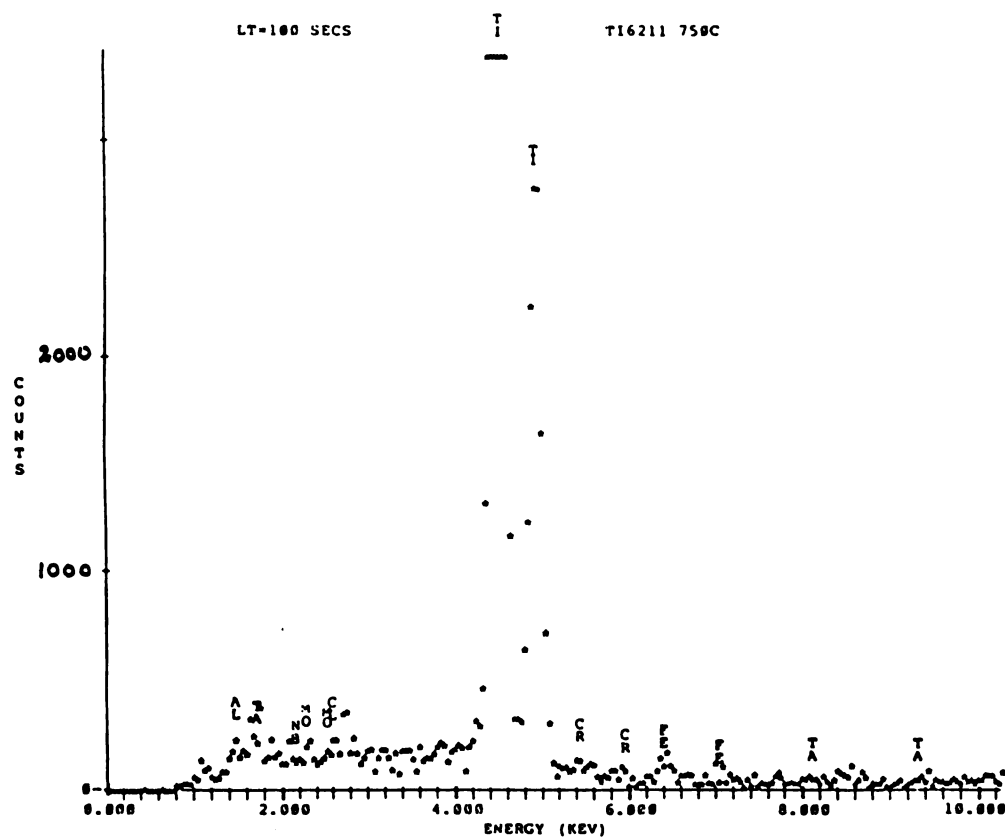


Fig.40. Microchemistry of 750°C specimen



Fig.39. SIEM micrograph of sample isothermally held at 750°C for one hour showing twins in martensite.



Fig.41. SIEM micrograph of sample isothermally held at 650°C for one hour showing beta.

of phases present at certain temperatures.

Fig 36 reveals a typical butterfly martensite showing two variants formed after 750°C isothermal treatment. This morphology of martensite has also been observed by other workers in this field. Fig 37 reveals acicular martensite with signs of twinning (temp 750°C). Figure 38, 39 clearly show the twinned region within the martensite. Results indicate that isothermal treatment at 750°C exhibit two morphologies of martensite as discussed. Solution partitioning tendencies at this temperature was studied by utilising energy dispersive analysis at a region within the martensitic plate as indicated. The EDS is taken for the plate shown in fig 33. Fig 40 corresponding to fig 39 shows that all the beta stabilising elements Ta, Mo, Nb are concentrated in this region with a comparatively low count of aluminum which is an alpha stabiliser but nevertheless is present in this alloy with a maximum weight percent constituent (6% wt). Fig 41 reveals an untransformed beta region, solution treated at 650°C and fig 42 reveals the microchemistry from a region within the plate. It is seen here that the partitioning of Nb, Mo, and Ta predominantly to beta phase increased as isothermal annealing temperature drops down to 650°C from 750°C. In general the diffusion rates of aluminum in beta is more sluggish than in alpha, because aluminum preferentially dissolves in the latter. Similarly the beta stabilising elements Mo, Nb, and Ta dissolve preferentially in the beta phase and their diffusion rates are higher in this phase.

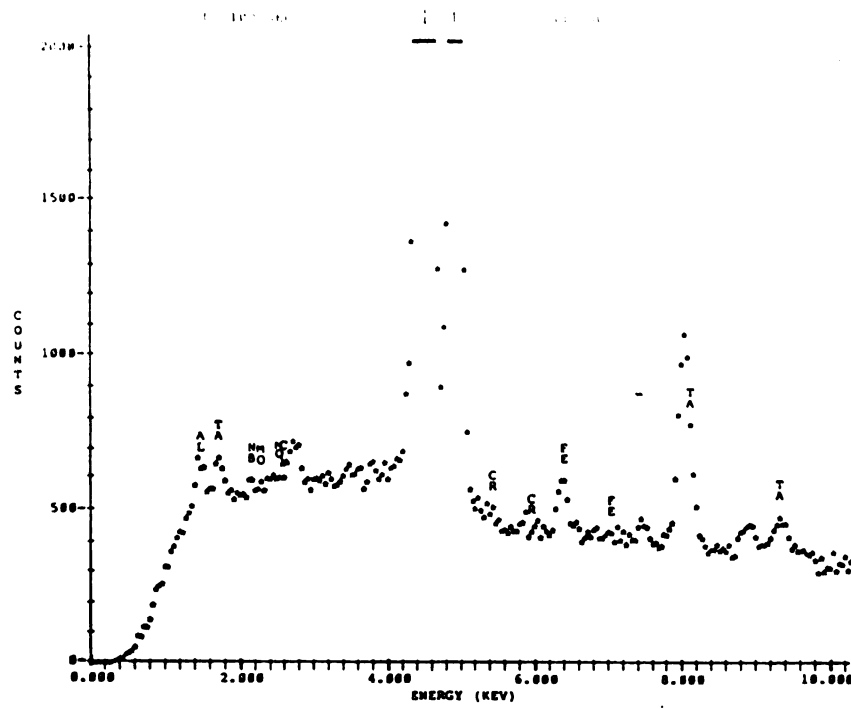


Fig.42. Energy Dispersive Analysis
of 650°C sample

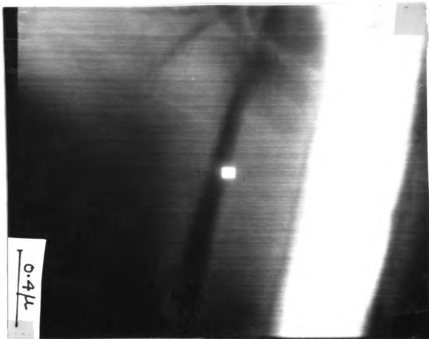


Fig.43. STEM micrograph of sample isothermally held at 800°C for one hour showing alpha plates and beta interface.

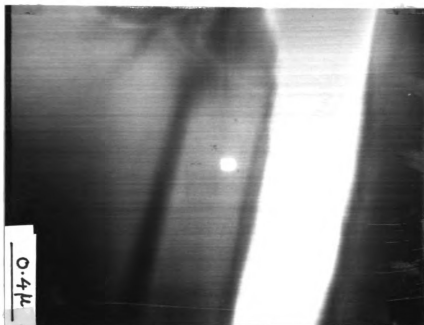


Fig.44. STEM micrograph of sample isothermally held at 800°C for one hour showing alpha plates.

As predicted in the schematic phase diagram of 6211 the solute concentration of beta phase should have a relatively wider range as compared to alpha phase, as one decreases the isothermal holding temperature. Figs 43, 44 reveal alpha platelets with an untransformed interface phase. Energy dispersive analysis was done at a region within the plate and also at a region near the interface as shown by the markers in Figs 43, 44. Fig 47, and fig 48 reflect microchemistries from a region within the plate and at the interface respectively. Within the plate it is seen that beta stabilising elements Mo, Nb, Ta are present at a much lesser concentration than aluminum whose counts are prominent. As we near the interface we find a drop in the concentration of aluminum, with the concentration of beta stabilising elements more or less being the same. This means that the interface is a region which rejects aluminum and encourages the dissolution of beta stabilising elements. There is a strong possibility of the interface being untransformed beta.

The same analysis was done for a specimen which was held isothermally at 700°C. Figs 49, 50 illustrate the regions where the analysis was done. Figures 51, 52 show the chemistries of the regions present. It is seen that there is a strong tantalum concentration as compared to the other alloying elements at this temperature within the beta platelets. The morphology of the platelets and solute concentration indicate the presence of beta region, and as we go towards the interface there is a drop in the tantalum and

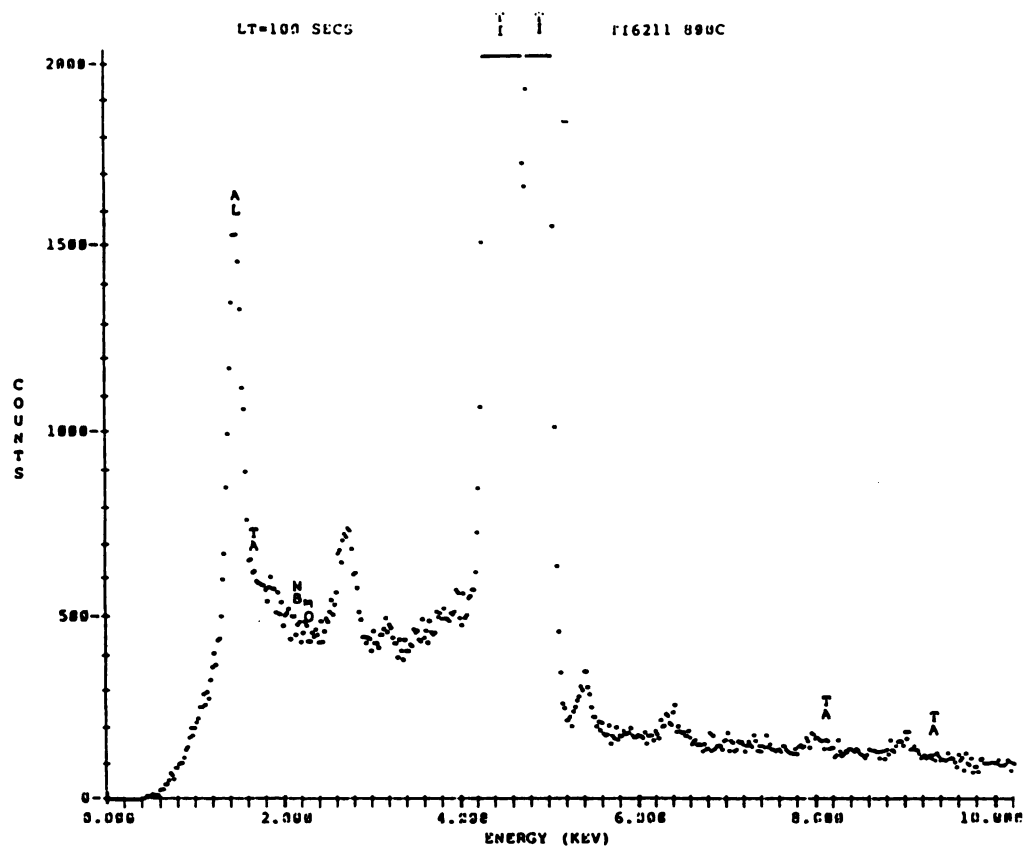
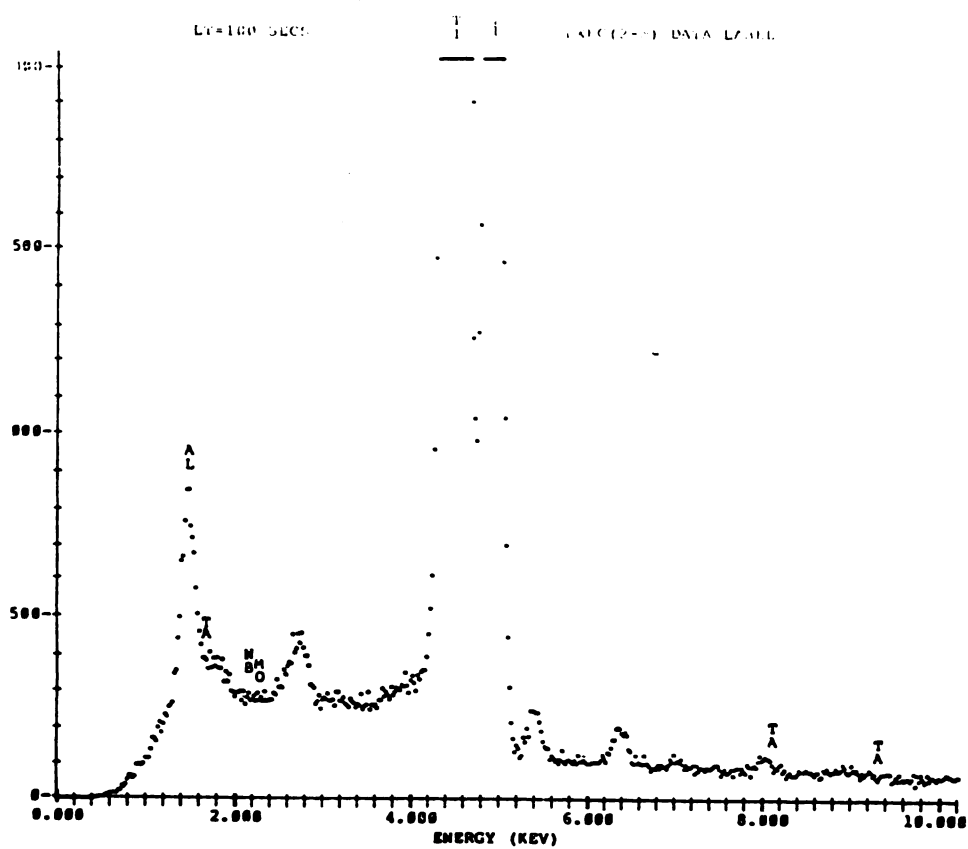


Fig.47. Energy Dispersive Analysis
of 800°C sample.



1 0.020KEV LT= 100SECS, LABEL:EXEC(2-W) DATA LABEL
 1.240: 1.740KEV GROSS= 12388 NET= 4588
 4.200: 5.260KEV GROSS= 327274 NET= 312382

Fig.48. Energy Dispersive Analysis
 of 800°C sample from the
 interface region.

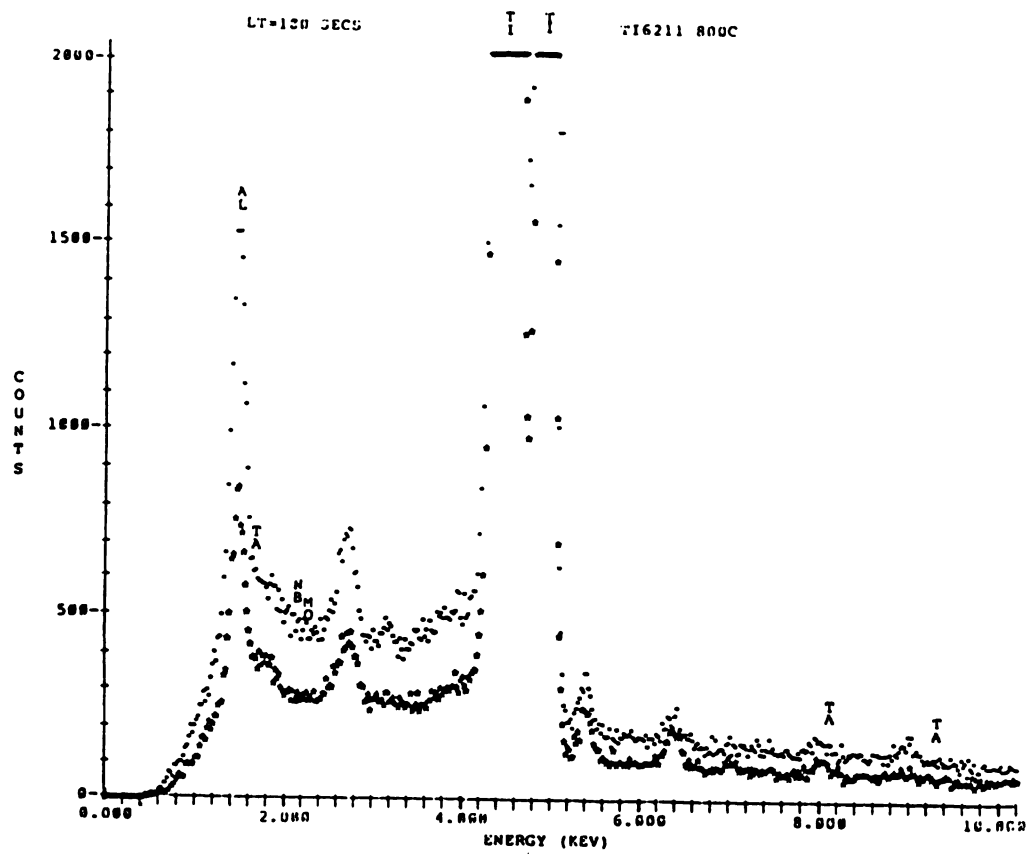


Fig.47 and Fig.48 superimposed.

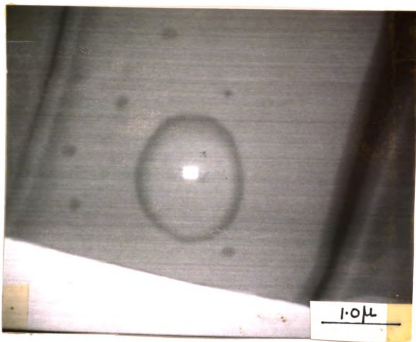
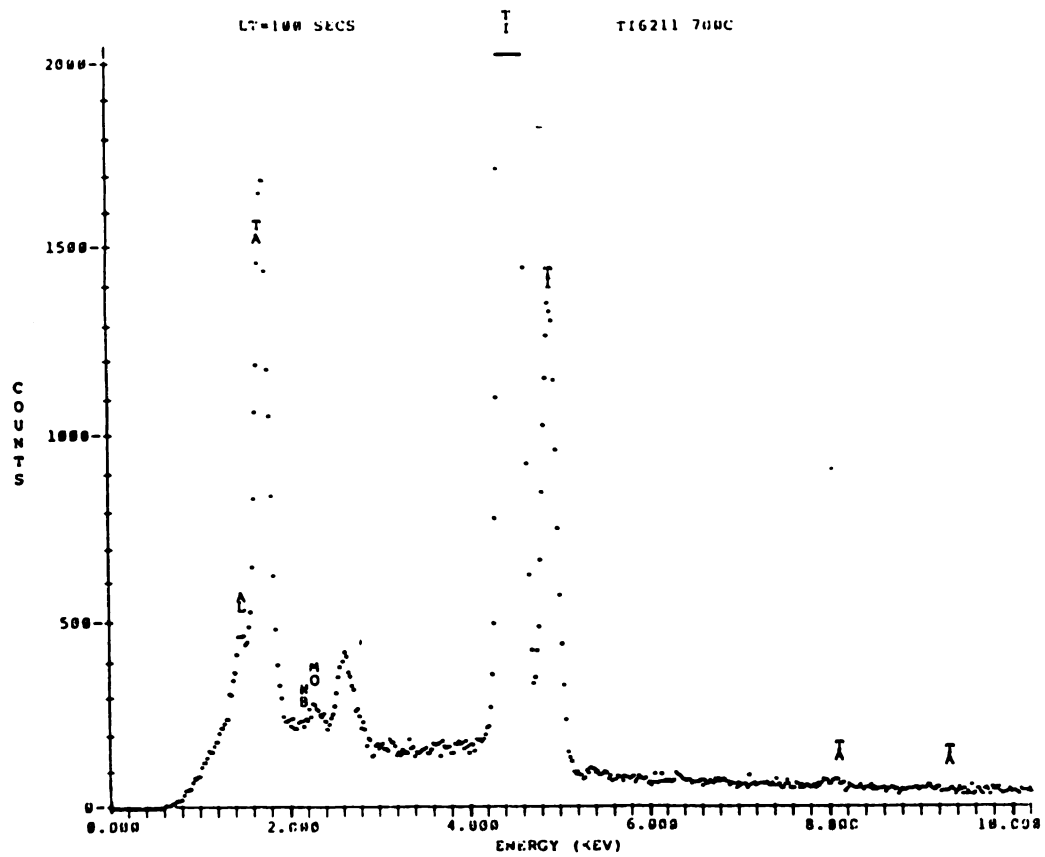


Fig.49. 700°C sample
showing region of
analysis



Fig.50. 700°C sample
showing interface
of analysis

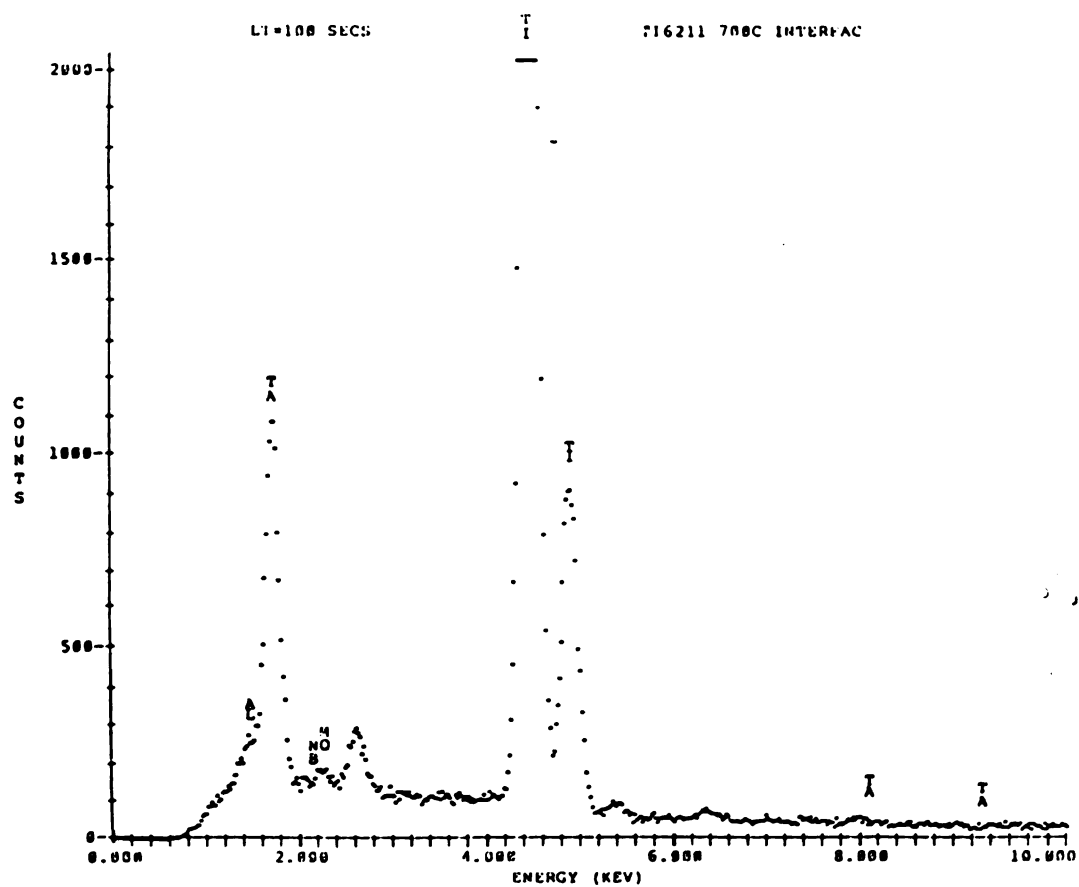


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REM 0 (12), 1 0.020KEV LT= 100SECS, LABEL:T16211 700C
REG 0 [00] 1.240: 1.740KEV GROSS= 15155 NET= -8545
REG 1 [01] 4.200: 5.260KEV GROSS= 100561 NET= 92452
REG 2 [02] 2.120: 2.640KEV GROSS= 1952 NET= 192
REG 3 [03] 1.520: 1.940KEV GROSS= 18695 NET= 18947

```

Fig.51. Energy Dispersive Analysis of 700°C specimen



MEM 0 (22), 1 0.020KEV LT= 100SECS, LABEL:T16211 700C INTERFAC

REG 0 [00]	1.240: 1.740KEV	GROSS=	9397	NET=	-5865
REG 1 [01]	4.200: 5.260KEV	GROSS=	59949	NET=	54437
REG 2 [02]	2.120: 2.460KEV	GROSS=	2546	NET=	234
REG 3 [03]	1.520: 1.940KEV	GROSS=	12109	NET=	7552

Fig.52. Energy Dispersive Analysis of specimen at interface, 700°C specimen.

aluminum concentration. The rejection of aluminum at the interface is consistent with the solute partitioning study done with the 800°C specimen. Studies indicate that in the temperature range 650°C-700°C there is a greater enrichment of tantalum in the beta region because of increased diffusion rates of tantalum in this temperature range.

5.3.1 Analyses of Ordering in Ti-6211

As discussed before, the phenomenon of ordering was investigated in this alloy using STEM techniques. Conventional TEM samples were used for analysis. Prior to making TEM samples, the alloy was subjected to 72 hours of aging at 450°C. Fig 53 reveals a typical alpha platelet with α_2 ordered precipitates. Fig 54 shows a magnified image of the α_2 ordered precipitates. It is clear that the precipitates are extremely fine i.e. less than 0.02 microns and can only be resolved under very high magnifications like 500,000 X. The precipitates are not strictly ellipsoidal but vary in size and morphology depending on local changes in misfit strain energy within the alpha matrix. Solute partitioning tendencies were studied in the ordered region and in a region other than the ordered precipitates signifying the average composition of the alloy. Figure 55 and fig. 56 reveal the microchemistry from a precipitate zone and an average zone respectively. The precipitate zone registered an aluminum count about 2.2 times that of the average matrix count. This is consistent with the fact that in the ordered structure (DO_{19} lattice) of composition Ti_3Al ,

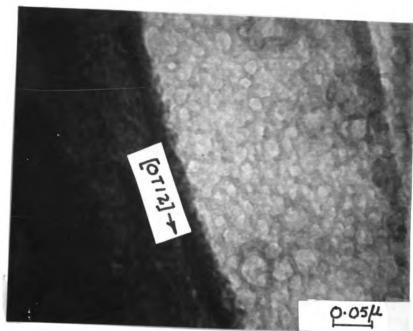


Fig.53. STEM micrograph of sample annealed at 450°C for 72 hours showing ordered precipitates.

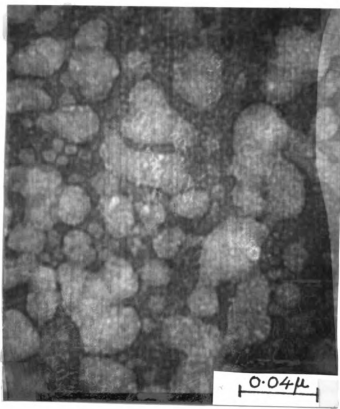
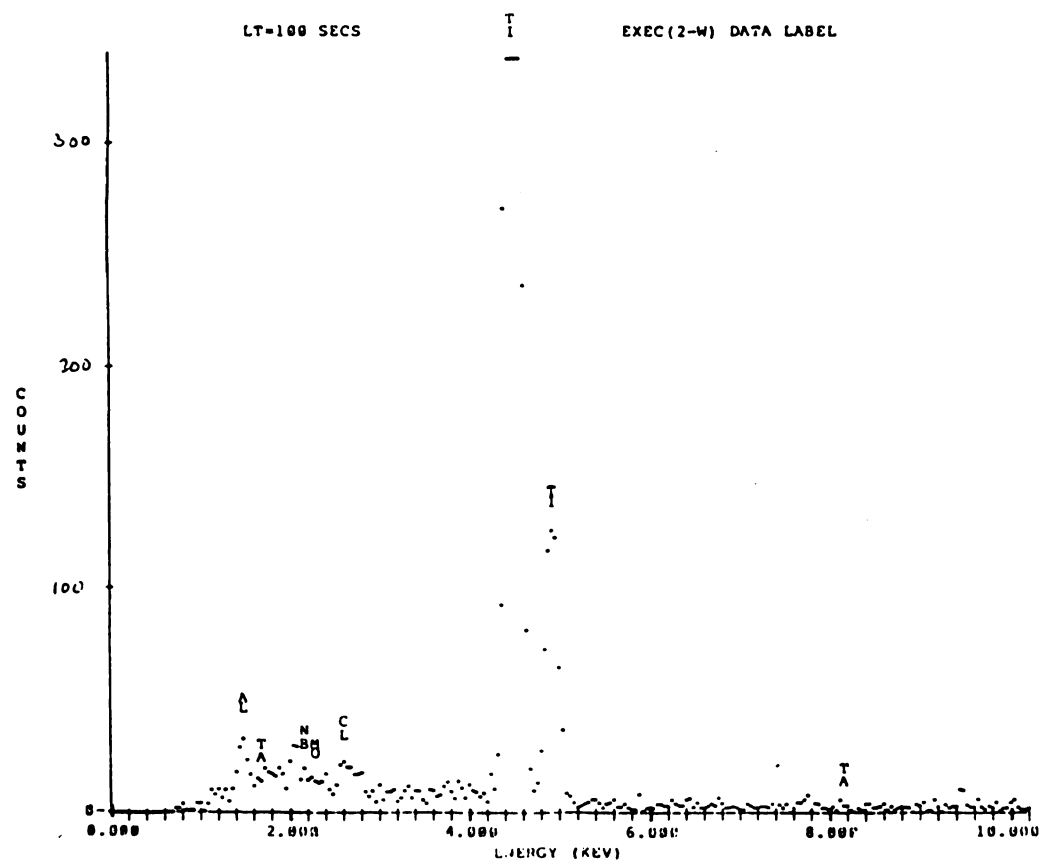


Fig.54 STEM micrograph showing magnified image of ordered α_2 precipitates.



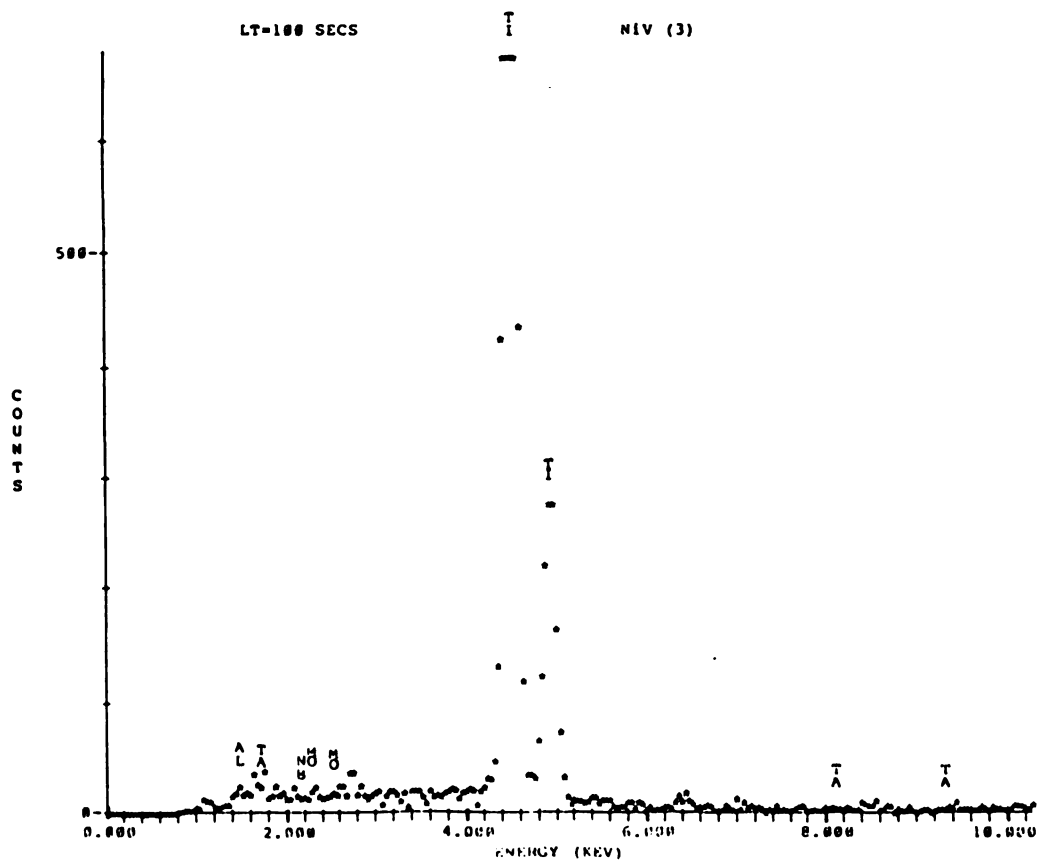


Fig.56. Energy Dispersive Analysis from region around α_2

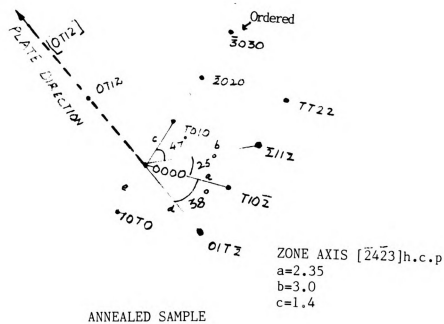
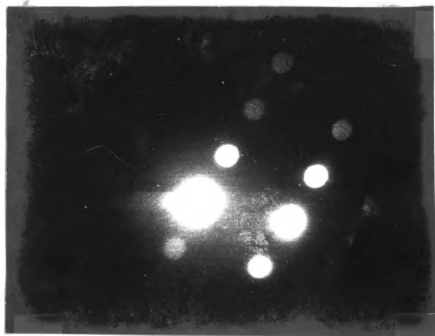


Fig.57. STEM picture showing microdiffraction from ordered α_2 precipitate zone.

aluminum occupies 25% of the total atomic concentration, as compared to the disordered alloy with an average random aluminum concentration of 10.44 at %. Microdiffraction in the precipitate region fig 57 revealed fundamental hcp spots along with superlattice spots i.e. spots which were not allowed in a hcp lattice according to the extinction rule. This further confirmed the α_2 ordered structure in this alloy. Further investigation of the α_2 structure is in progress using differential scanning calorimetric techniques (DSC).

5.4 Summary and Conclusions

1. TEM studies show that hexagonal martensite forms on quenching from higher isothermal holding temperatures of 900-950°C, and on progressively going down in the isothermal holding temperatures, there is a tendency for beta to remain untransformed.
2. As isothermal holding temperature decreases the morphology of alpha platelets assume a Widmanstätten shape.
3. The amount of equilibrium alpha increases at lower isothermal holding temperatures.
4. The interface phase is stable in the 750°C-850°C range.
5. Solute partitioning tendencies in this alloy indicate a greater concentration of beta stabilising elements at lower isothermal holding temperatures. The temperature range 650°C-700°C encourages a greater tantalum enrichment in the beta phase, because of increased diffusion rates of tantalum.

6. There is a marked drop in the concentration of beta stabilising elements as one goes away from the interface region towards the center of the transformed beta product, indicating that the interface region has the composition of untransformed beta.
7. Ti-6211 exhibits ordering at 450°C aging, leading to fine ellipsoidal α_2 precipitates of Ti_3Al composition and DO_{19} structure. Further investigation is in progress using Differential Scanning Calorimeter (D.S.C.) techniques.

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