It is well known that mechanical and physical properties of titanium and its alloys are dependent sensitively upon the presence of interstitial elements like carbon, nitrogen and oxygen. Among these nitrogen is an effective stabiliser of the hexagonal closepacked $\alpha$-titanium, in addition to imparting maximum strength to titanium and its alloys. The Ti-N system has not been studied in detail as compared to Ti-O and Ti-C systems. Considering the atom size of nitrogen solute against the typical octahedral void size of $\alpha$-titanium, there exists a certain probability of distortion of the host lattice. Consequent strain energy contribution, influences the overall stability of the various phases that could form in Ti-N system by various decomposition processes. The increase in the strain energy of the lattice caused by the occupation of interstitials, results in two significant effects: (i) nitrogen solubility is severely restricted and (ii) even with the low solubility an ordering of nitrogen in the lattice is favoured. The present study is aimed at understanding the ordering of nitrogen atoms in hcp titanium and the subsequent precipitation of $\text{TiN}_x$ ($\alpha'$) tetragonal phase from the supersaturated matrix. Further the study has been extended to examine the role of nitrogen on the phase transformations that occur in binary Ti-Fe alloys.

Thin foils of 25-50 $\mu$m thickness of titanium, Ti-2a/o, 6a/o Fe were nitrided in flowing ultra high purity nitrogen gas in the $\alpha$-phase fields and quenched from the $\beta$-phase regions of the respective alloys. Some of the Ti-1.6a/o N
alloy samples were aged in the temperature interval 300-673 K for various durations extending up to 50 hours. Both the quenching and ageing treatments were done in a vacuum better than $10^{-3}$ Pa. $T_c$ measurements were carried out for both quenched and aged conditions of Ti-N alloys resistively using a four probe technique in a conventional liquid helium exchange gas cryostat. Both conventional transmission electron microscopy and high resolution electron microscopy were carried out to characterise the phase transformations occurring in the systems.

The energetics of interstitial ordering has been analysed using a quasi-chemical approach incorporating interactions up to second nearest neighbours. A nitrogen housing scheme has been proposed with a view to minimise the strong coulombic repulsion and to offer minimum lattice distortions. Modelling on this basis, it is found that the combined effect of first and second near neighbour interactions gives rise to the formation of ordered superstructures. A martensitic transformation of the ordered domains is predicted around the composition of 16 a/o nitrogen, as a result of the stress field associated with the interstitial atoms.

The early stages of the decomposition of the supersaturated $\alpha''$ phase which was obtained on quenching the Ti-1.6a/O N alloy have been found to be associated with characteristic microstructural features. The tetragonally ordered $\alpha'$ phase formed from $\alpha''$ by continuous ordering, transforms to incoherent Ti$_2$N precipitates on ageing in the
temperature range 323-673 K. While no perceptible growth of homogeneously transformed \( \alpha' \) phase is observed in the matrix, lath boundary precipitation of \( \alpha'/\text{Ti}_2\text{N} \) occurs during low temperature ageing (\( T < 373 \text{K} \)). On ageing at high temperatures (\( T > 373 \text{K} \)) both matrix and lath boundary precipitation of \( \text{Ti}_2\text{N} \) take place uniformly by nucleation and growth process.

The orientation relationship between the \( \alpha'' \) and \( \alpha' \) phases has been identified as

\[
(1 0 1 0)_{\alpha''} \parallel (0 1 1)_{\alpha'} \\
[1 1 1 0]_{\alpha''} \parallel [0 1 1]_{\alpha'}
\]

The experimental results obtained on the precipitation of \( \text{Ti}_2\text{N} \) from supersaturated \( \alpha'' \) phase suggest that the transformation \( \alpha'' \rightarrow \text{TiN}_X \ (X \sim 0.2 - 0.5) \) has been shown to satisfy the invariant plane strain conditions (IPS).

High resolution images were obtained in both the quenched and aged samples of the Ti-1.6 a/o N alloy. Images have been interpreted using the geometrical projection of atoms from the anti-rutile \( \text{Ti}_2\text{N} \) structure. On comparing the simulated and actual high resolution image it is concluded that only Ti-atoms are imaged as white dots. The interfaces between the \( \alpha/\alpha' \) phases remain coherent in the quenched condition of the alloy, while they become incoherent on continuous precipitation of nitrogen atoms, from the matrix.

It is inferred that the disordered supersaturated \( \alpha'' \) transforms to \( \text{Ti}_2\text{N} \) by the following predominant reaction
sequences;

(i) \( \alpha'' \rightarrow \alpha + \alpha' \rightarrow \alpha + \text{Ti}_2\text{N} \) by continuous ordering at \( T < 473 \text{ K} \)

(ii) \( \alpha'' \rightarrow \alpha + \text{Ti}_2\text{N} \) by heterogeneous nucleation and growth at \( T > 473 \text{ K} \)

In a concurrent study, Ti-Fe (2 and 6% Fe) alloys have been investigated to understand critically the nature of martensitic and omega reactions. In the light of the studies in Ti-N system, it is expected that nitrogen solute would have a significant influence on these reactions. Optical metallography revealed the presence of hexagonal \( \alpha_1' \) phase in a matrix of retained \( \beta \) phase on quenching the Ti-6% a/o Fe alloy. The hexagonal \( \alpha_1' \) phase exhibited two distinct morphologies—one obeying Burger's orientation relation and the other not conforming to any specific orientation relation. The retained \( \beta \) phase showed the existence of dynamical omega fluctuations as well as the presence of fine scale omega phase precipitation. The nitrogen bearing Ti-6% a/o Fe alloy on quenching at comparable rates produced only Burger's oriented martensite plates and no retained \( \beta \) phase could be detected. In other words, the nitrogen additions seem to inhibit the \( \beta \rightarrow \beta + \omega \) reaction while promoting the \( \beta \rightarrow \alpha_1' \) reaction.

Many of the nitrogen martensite colonies in both the Ti-2% Fe-2% N and Ti-6% Fe-1.5% N alloys have shown signs of initial stages of decomposition, exhibiting features
similar to that obtained in Ti-1.6 a/o N alloy. Electron diffraction analyses confirm that the product microstructure possesses the tetragonal Ti$_2$N structure. The experimental observations along with the theoretical predictions on nitrogen ordering behaviour suggest, that the reactions in interstitial alloys proceed frequently stepwise till it reaches equilibrium composition. In the process, the system minimises the total energy by local rearrangements to form a variety of metastable ordered phases.

Titanium on quenching from the β phase regions does not show superconducting transition down to 1.6K is well known. Interestingly all the titanium-nitrogen alloys exhibited enhancement in superconducting transition temperature T$_c$ and for any concentration up to 2a/o N, T$_c$ is at its highest value in the β quenched state of the alloy i.e. ~3K. It has been noticed that a degradation in T$_c$ occurs due to ageing the alloy at higher temperatures. It has been found that the samples are restored to normal state after 10 hours of ageing at 473K. Thus it is demonstrated that the superconducting parameter T$_c$ is sensitive to microstructure. The phenomenon investigated was examined in detail from various angles like nitrogen ordering, precipitation behaviour and microstructural characteristics and the findings of the examination are adopted to provide a physical basis for the observed superconductivity in dilute nitrogen alloys of titanium. The well known mechanisms like proximity effect and the effect of dislocations do not satisfactorily explain the observed enhancement of T$_c$. Various other
approaches/models like Kulik layer model and retained $\beta$ effect were also examined for explaining the phenomenon. In the absence of a satisfactory explanation from the existing approaches/models, a new approach has been proposed, namely the "Strain field criterion", to explain the superconductivity behaviour. The strain field criterion suggests that the strain field distribution associated with the precipitate/matrix interfaces could be responsible for the enhanced $T_c$. The strain field dependence on ageing has to be taken into account while interpreting the anomalous behaviour of superconductivity. The high resolution electron microscopy work carried out in the Ti-1.6a/o N alloy lends support to the above mentioned view.

The major conclusions of the work are summarised below:

(1) Theoretical studies on the energetics of the ordering of N-atoms and precipitation indicate that there exists a critical concentration around 16 a/o N beyond which hexagonal structure of $\alpha$-Ti is rendered unstable.

(2) The structural transformation from hexagonal to tetragonal (anti-rutile structure) takes place martensitically and the microscopic strain associated with the transformation $\alpha$ $\rightarrow$ TiN$_x$ ($x \approx 0.2 - 0.5$) is shown to satisfy the IPS conditions.

(3) Precipitation of the second phase in Ti-Fe-N alloys with a tetragonal structure follows a similar sequence observed in dilute Ti-N alloys.
The actual $T_c$ values have been found to be strongly dependent upon the N-concentration and microstructure. The strain field criterion suggests the dependence of $T_c$ on the nature and distribution of the strain field patterns in and around the coherent interphases of $\alpha$ and $\alpha'$. When the strain field interaction ceases to be longrange in nature, degradation in $T_c$ is noticed.