Chapter 10

Summary, conclusions and future outlook of the study

10.1   Summary and conclusions

In this thesis we have presented an experimental study on four Ti_xV_{1-x} alloys having concentrations $x = 0.8$, 0.7, 0.6 and 0.4. This study was focused to understand the structural properties as well as various important superconducting and normal state properties of these Ti-V alloys. The structural properties are studied through X-Ray diffraction (XRD) experiments (using both laboratory based and Synchrotron radiation sources) and optical metallography. The properties of the Ti-V alloys in their normal as well as superconducting state are studied through the measurements of resistivity, magnetization, and the heat capacity as functions of temperature and magnetic field. In this study, we have also attempted to investigate on how the structural and the normal state properties influence the superconducting properties of these Ti-V alloys. In this chapter we present the overall

summary and the conclusions of this study.

The XRD patterns of the Ti-V alloys were analysed using the Rietveld refinement technique to find out the crystal structure as well as the volume fractions of the constituent phases present in the alloys. The analysis of the XRD results indicates that the present Ti-V alloys are formed predominantly in body-centre-cubic (bcc) β phase crystal structure. Apart from the major β phase, the Ti-V alloys also contain hexagonal ω phase as well as martensite α and α' phases. The martensite α phase has a hexagonal closed packed crystal structure. This phase is formed in a considerably large amount ($\sim$28 %) in annealed $Ti_{0.7}V_{0.3}$ alloy while a small amount of this phase ($\sim$2 %) is also detected in the annealed $Ti_{0.4}V_{0.6}$ alloy. On the other hand, the martensite α' phase is present in both the annealed and as cast samples of the $Ti_{0.8}V_{0.2}$ alloy. This martensite α' phase has an orthorhombic crystal structure, and is known to be formed due to a stress induced athermal transformation of the β phase [58, 107, 108].

Optical micrographs show that these polycrystalline Ti-V alloys have very large β phase grains with average grain size ranging from few tens to few hundreds of micron. Apart from the signature of grain boundaries, a dotted microstructure is also visible to be densely distributed over the β phase matrix of few samples of the present Ti-V alloys. In some portion of these samples, the dotted microstructures show a tendency to lining-up, which is reported to indicate the presence of edge dislocations and low angle grain boundaries inside the β phase matrix of these sample [37]. Optical micrographs of the

annealed samples of the $Ti_{0.7}V_{0.3}$ and $Ti_{0.4}V_{0.6}$ alloys show that the martensite α phase mostly formed in needle shaped pattern, is inhomogeneously distributed within the β phase matrix of these alloys. On the other hand, the stress induced martensite α' phase in both annealed and as cast samples of the $Ti_{0.8}V_{0.2}$ alloy is formed in the shape of needles near the edges of these samples. It was inferred that the α' phase is formed during the mechanical processing such as cutting of the sample [110].

We have estimated the superconducting transition temperature T_C, various critical fields (the upper critical field H_{C2}, the lower critical field H_{C1}, and the thermodynamic critical field H_C), the coherence length ξ, the magnetic field penetration depath λ, and the Ginzburg-Landau parameter κ to characterize superconducting state properties of the present Ti-V alloys. We have also estimated the Debye temperature θ_D and the electron-phonon coupling constant λ_{ep} from the low temperature heat capacity data, and the bare electronic density of states at the Fermi energy $N(0)$ obtained from the band structure calculation. The estimated values of λ_{ep} have led us to infer that the Ti-rich Ti-V alloys are weak-coupling superconductors. As the Ti concentration is decreased, λ_{ep} increases and becomes ~ 1 for the $Ti_{0.4}V_{0.6}$ alloy, indicating the moderate to strong coupling nature of superconductivity in the V-rich Ti-V alloys. Then we have compared the experimentally determined T_C values with those obtained using McMillan formula [19]. The T_C value thus estimated is found to be much higher than the experimentally determined value for the Ti_xV_{1-x} alloys with $x = 0.4$, 0.6 and 0.7.

It was found that Pauli paramagnetic pair-breaking effect [128, 129] imposes limitation on the experimental H_{C2} in the Ti-rich Ti-V alloy superconductors. However, enhanced electron-phonon interaction in the V-rich Ti-V alloys (as indicated by the increased value of λ_{ep} with increasing V concentration in the Ti-V alloys) reduces the role of the Pauli paramagnetic pair-breaking effect, and thereby the experimentally determined H_{C2} in the V-rich Ti-V superconductors agrees well with the prediction of the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory [8, 20].

The field dependence of magnetization curve of few samples of the present Ti-V alloys particularly those having relatively low density of defect structures, bears some signature for the presence of Bean-Livingston surface barrier [26]. However, we have found that in the present Ti-V alloy superconductors the existence of the Bean-Livingston surface barrier does not raise the characteristic field for the first flux-line penetration H_P above the lower critical field H_{C1}. The existence of the Bean-Livingston surface barrier only lowers the rate of flux-line penetration in these samples. The Ginzburg-Landau parameter κ was estimated and found to be very high for these Ti-V alloy superconductors, indicating that these superconductors are extreme type-II superconductors. The κ value increases progressively from 32 to 55 as the Ti concentration is increased from $x = 0.4$ to 0.8 in the Ti_xV_{1-x} alloys. From the knowledge of the estimated superconducting parameters, we have inferred that the flux-line lattice in the V-rich Ti-V alloys is more rigid as compared to that in the Ti-rich alloys. This is important information has

implications on the current carrying aspect of these superconductors.

Superconducting fluctuations induced conductivity in the annealed Ti-V alloys above the superconducting transition temperature T_C has been studied through the measurements of electrical resistivity as functions of temperature and magnetic field. All the currently investigated Ti-V alloys exhibit a strong rounding-off behaviour in the resistive transition, and the trace of this behaviour persists up to the temperature $\sim 2T_C$. Moreover, these Ti-V alloys exhibit strong positive magneto-resistance in the same temperature regime where the experimental observation of the excess conductivity is possible within the level of experimental accuracy. Aslamazov-Larkin theoretical model [157] and its extended version [158] consistently describe the excess conductivity data of the present Ti-V alloys. In order to explain the strong positive magneto-resistance observed in the temperature range from T_C to $2T_C$, we have invoked the theoretical model of Usadel [159] which considers the magneto-resistance associated with the Aslamazov-Larkin superconducting fluctuations induced conductivity. We have found that this theoretical model consistently describes the magnetic field dependence of the magneto-resistivity of the Ti-V alloys. Based on these observations we have inferred that the rounding-off behaviour of the resistive transition in the Ti-V alloys occurs due to enhanced role of the superconducting fluctuations in these alloys. The Ginzburg number G_i for the Ti-V superconductors is estimated and found to be $\sim 10^{-6}$-10^{-5}, which is intermediate between those for high-T_C cuprate superconductors ($G_i \sim 10^{-2}$) and conventional low-T_C superconduc-

tors ($G_i \sim 10^{-8}$). We have suggested that the moderate value of G_i of the Ti-V superconductors makes the superconducting fluctuations significant in the experimentally accessible temperature window in the present bulk low-T_C superconductors. Hence, the outcomes of the present study resolve the debated problem of the observed rounding-off behaviour of the resistive transition in the Ti-V alloys, for which both the superconducting fluctuations [85-87] and the spin fluctuations [44, 88, 94] scenario were independently proposed previously.

Physical properties such as electric resistivity, magnetization, and heat capacity of Ti-V alloys are studied in the normal state of the Ti-V alloys. The important properties of the Ti-V alloys in their normal state are:

(i) The considerations of only the electronic and the Debye lattice heat capacity cannot explain the experimental temperature dependence of heat capacity data in the wide temperature range 10-225 K. At lower temperature regime, the experimental heat capacity data deviate from the fitting performed by considering only the electronic and the Debye lattice heat capacity.

(ii) A non-linearity with a negative curvature is observed in the plots of C/T as a function of T^2 at low temperatures.

(iii) Dc magnetic susceptibility follows $-T^2 lnT$ dependence on temperature.

(iv) There is an enhancement of the stoner factor S in $Ti_x V_{1-x}$ alloys with $x \leq 0.7$.

(v) For the $Ti_{0.4}V_{0.6}$ and $Ti_{0.6}V_{0.4}$ alloys, the electrical resistivity varies with temperature as $\rho(T) = \rho_0 + AT^2 + BT^5$ at low temperatures. The coefficient of the T^5 term in low-temperature resistivity is found to be very small. This coefficient is positive for the $Ti_{0.4}V_{0.6}$ alloy and negative for the $Ti_{0.6}V_{0.4}$ alloy.

(vi) For the $Ti_{0.4}V_{0.6}$ and $Ti_{0.6}V_{0.4}$ alloys, the Somerfield coefficient γ and the coefficient A of the T^2 term in the temperature dependence of electrical resistivity at low temperatures follow the KadowakiWoods relation, according to which $A/\gamma^2 = 1.0 \times 10^{-4}$ $\mu\Omega$-cm(mole/mJ)^2 for the spin fluctuating systems [180].

All the above characteristic features pointed out above uniquely imply that spin fluctuations are important in the Ti-V alloys particularly in those having high V concentration [155, 156]. The outcome of this study was then used to resolve the problem of the observed disagreement between the experimentally measured and the theoretically predicted T_C values of the Ti_xV_{1-x} alloys with $x \leq 0.7$. We have suggested that spin fluctuations, whose presence is evident in various normal state properties of the Ti-V alloys, suppress the T_C from a much higher value $\sim$15-20 K (as calculated using McMillan formula) to the experimental value which is less than 8 K for the Ti_xV_{1-x} alloys with $x \leq 0.7$ [155, 156].

From the point of practical applications, the critical current density J_C in as cast and annealed samples of the Ti-V alloys has been studied in detail. J_C is estimated from the irreversible magnetization using Bean's critical state

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model [27]. As cast $Ti_{0.7}V_{0.3}$ alloy has the highest J_C value among all the investigated alloys. To understand the flux-line pinning mechanisms operating in the present Ti-V superconducting alloys, a detailed analysis of the field dependence of pinning force density $F_P(= J_C \times H)$ has been performed using Dew-Hughes model [213]. Flux-line pinning at normal surface pins has the major contribution to the pinning force density in all the as cast and annealed Ti-V alloys except in the annealed $Ti_{0.8}V_{0.2}$ alloy. The grain boundaries and edge dislocations seem to constitute the sources of such normal surface pinning centres in these alloys. In the annealed $Ti_{0.8}V_{0.2}$ alloy, flux-line pinning occurs predominantly at normal point pins while the role of normal surface pins is prevalent at relatively lower magnetic field. Substantial amount of the ω phase available in this sample functions as the normal point pinning centres. In the present Ti-V alloys, the most relevant pinning centres such as grain boundaries have length scales of the order of few tens to few hundreds of micron while inter-spacing between flux lines is of the order of few tens of nm for an applied magnetic field of only 1 T, implying the lack of sufficient pinning centres in these alloys. In spite of this fact, the zero field J_C value obtained in the as cast $Ti_{0.7}V_{0.3}$ alloy is only one order of magnitude lower than that obtained in Nb-Ti superconducting wires which is extensively used in the fabrication of high-field magnets (as cast $Ti_{0.7}V_{0.3}$ superconductor: $J_C(H = 0 \text{ T}, T = 4.2 \text{ K}) \sim 7 \times 10^8 \text{ A/m}^2$; Nb-Ti superconductor: $J_C(H = 0 \text{ T}, T = 4.2 \text{ K}) \sim 10^{10} \text{ A/m}^2$ [25]). Therefore, there is an ample scope to achieve a sufficiently high level of J_C in the Ti-V alloy superconductors by

artificially introducing disorders in these materials.

We have further investigated on how the intrinsic superconducting properties of the Ti-V alloys govern the flux-line pinning properties in the same. In these Ti-V alloys, J_C drops sharply in high magnetic field regime and vanishes at the irreversibility field H_{Irr} which is distinctly different from H_{C2} in these alloys. The limitation of J_C in high magnetic field regime was inferred to occur due to the thermal fluctuation effect, as is the case for the high-T_C superconductors. As the value of Ginzburg number G_i decreases with decreasing Ti concentration in the Ti-V alloys, thermal fluctuation effect becomes gradually less important in the V-rich Ti-V alloys. Consequently, the V-rich Ti-V alloys exhibit relatively improved high-field J_C behaviour. So our study shows that **from the J_C point of view the V-rich Ti-V alloys are superior than the Ti-rich Ti-V alloys**.

We have also studied the peak-effect observed in all the annealed and as cast Ti-V alloys except the annealed $Ti_{0.7}V_{0.3}$ alloy. The peak-effect is characterized by an abrupt enhancement of the irreversible magnetization (and hence critical current J_C) in high magnetic field regime below H_{C2}. To investigate into the origin of the peak-effect, we have constructed the minor hysteresis loops (MHLs) in and around the peak-effect regime. Magnetic hysteresis of these Ti-V alloys shows history effects within the peak-effect regime, which are known to be characteristic features related to the meta-stability (super heating/supercooling) associated with a first-order phase transition in the flux-line system [218-220]. We have then estimated equilibrium mag-

netization (M_{eq}) at different magnetic field from these MHLs. The magnetic field dependence of M_{eq} shows a clear jump within the peak-effect regime, which again indicates the first-order nature of the stated phase transition. We have suggested that a disorder-driven phase transition in the flux-line system gives rise to the peak-effect in the present Ti-V alloys.

We have presented a study on the vortex-glass to vortex-liquid phase transition in the flux-line system of the annealed $Ti_{0.7}V_{0.3}$ alloy. In order to ascertain the existence of such a phase transition in the flux-line system, the superconducting transition in this alloy has been studied thorough resistivity measurements in the presence of various constant applied magnetic fields, and the results are analyzed based on the theory of vortex-glass [38-41] as well as the modified vortex-glass model [247, 248]. We have estimated the glass transition temperature T_G and the critical exponent s for the vortex-liquid to vortex-glass phase transition. The s value is found to be ∼1.8 and is almost independent of magnetic field. From both the estimated values of s as well as the nature of the disorders present in this sample, it is inferred that a Bose-glass [40, 41] vortex phase is formed in the mixed state of the annealed $Ti_{0.7}V_{0.3}$ alloy. We have estimated the activation energy or the effective pinning energy U_0 for the annealed $Ti_{0.7}V_{0.3}$ alloy using the modified vortex-glass model [247, 248]. Both the temperature and magnetic field dependencies of U_0 in the annealed $Ti_{0.7}V_{0.3}$ alloy are found to be distinctly different in the magnetic field regimes below and above 2 T, and these features are attributed due to the crossover from individual vortex pinning

regime to the collective pinning regime. For higher magnetic field (above 2 T), the temperature and magnetic field dependencies of U_0 of the annealed $Ti_{0.7}V_{0.3}$ alloy were found to be qualitatively very similar to those predicted for the high-T_C superconductors [247, 248]. Consequently, in this magnetic field regime, the vortex-liquid resistivity of the annealed $Ti_{0.7}V_{0.3}$ alloy in the critical region of the vortex-liquid to Bose-glass phase transition has been observed to follow the scaling behaviour predicted by the modified vortex-glass model [247, 248]. However, the same scaling law referred above was found to be not valid in low magnetic field regime. We have proposed a new scaling law for the vortex-liquid resistivity for low magnetic field regime. The vortex-liquid resistivity of the annealed $Ti_{0.7}V_{0.3}$ alloy in low magnetic field regime has been found to follow this new scaling law. This is the first study showing the scaling behaviour of the vortex-liquid resistivity in a low-T_C superconductor.

We have studied the high-field paramagnetic effect (HFPME) in as cast and annealed samples of $Ti_{0.8}V_{0.2}$ alloy and annealed sample of $Ti_{0.7}V_{0.3}$ alloy. In presence of relatively higher magnetic field (of the order of 1 Tesla), FCC magnetization of these multiphase Ti-V samples increases when temperature is decreased well below T_C. Moreover, in the superconducting state, FCW magnetization is found to be larger than the FCC magnetization. The FCW magnetization in the superconducting state even becomes larger than the normal state magnetization. These observed magnetic behaviours are distinctly different from the conventional magnetic responses of a type-II su-

perconductor, and are known as characteristics of the HFPME [291-296]. We have suggested that the inhomogeneous distribution of flux lines driven by the flux-line pinning at α (or α') phase regions is the essential mechanism leading to the observed HFPME in these samples. The above interpretation has been tested and confirmed by observing the complete disappearance of the HFPME in a $Ti_{0.8}V_{0.2}$ sample from which α' phase is removed by annealing it at an elevated β-field temperature. FCC magnetization exhibits strong dependence on both time as well as the temperature sweep rate of the measurements. Based on these experimental results, we have recognized the flux-creep effect as an important ingredient for the occurrence of the HFPME. We have interpreted that the creep of the flux lines into some stronger pinning centres available in these alloys (α or α' phase in these Ti-rich Ti-V alloys) enhances the flux-line density at these pinning centres, and thereby giving rise to the increase in paramagnetic response of the samples with time. We have also found that the coherence length ξ is another important factor, which governs the strength of the HFPME in a superconductor. These factors referred above successfully explain all the characteristic features associated with the HFPME exhibited by the present Ti-V alloys as well as many other superconducting systems.

10.2 Future outlook

One of the important outcomes of the present study is that the superconducting transition temperature T_C of the Ti-V alloys is significantly reduced due to the presence of spin fluctuations in these alloys. This result provides a way to achieve significantly higher T_C values up to $\sim$15-20 K for the Ti-V alloys by suppressing the role of spin fluctuations in these alloys. The doping of a third element with negligible influence of spin fluctuations into the Ti-V alloys by not perturbing the electronic band structure remarkably could be a possible technique for the T_C enhancement. However, the malleability, which is known to be one of the important merits of the Ti-V superconductors for being used in technological applications, should not be compromised by such T_C enhancement process. The origin of spin fluctuations in the Ti-V alloys is itself an interesting research problem which is yet to be answered properly.

While investigating on the critical current aspect of the present Ti-V alloys, we have found that the there is an ample scope to achieve a sufficiently high level of J_C in the Ti-V superconducting alloys by artificially introducing disorders in these alloys. In this direction, we have planned to introduce disorders in the present Ti-V alloys by heavy ion irradiation technique which is known to be one of the promising techniques for the improvement of the critical current density. Currently, this work is in ongoing stage.

Moreover, in this thesis, a little effort has been put to study the peak-effect phenomenon, which is observed quite often in the Ti-V alloys as well

as many other Ti-based transition metal alloys. To obtain a more complete and comprehensive picture of this phenomenon, we are now studying this phenomenon in detail.