CHAPTER VII
SUMMARY AND CONCLUSION

The thesis presents a detailed investigation on the phase transformations in Ti$_3$Al and Ti$_2$ZrAl intermetallic alloys induced by hydrogenation and irradiation. This chapter summarises important results and also discusses the future scope of investigation in this area.

The single-phase intermetallic alloys Ti$_3$Al and Ti$_2$ZrAl were arc melted and characterized by various techniques like Powder X-ray Diffraction (XRD), Electron Probe Micro Analysis (EPMA), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and it was found as single phase. The single-phase alloys were polished mechanically for the hydrogenation and irradiation studies. For Ti$_2$ZrAl, crystallographic structure was determined and it is found to be having the same structure of Ti$_3$Al, where Zr randomly occupies the Ti position with different occupancy in the unit cell having space group P6$_3$/mmc. As no data was available with the Joint Committee on Powder Diffraction Standards (JCPDS) on the XRD analysis of Ti$_2$ZrAl, the findings from the present investigations was presented to the International Centre for Diffraction Data (ICDD) and it has been published in Powder Diffraction Journal.

Hydrogenation was done on the samples by cathodic charging method and gas phase hydrogen charging method. The two different methods of charging resulted in different hydride phases. Initially the samples were hydrogenated by cathodic charging method with 0.1N H$_2$SO$_4$ and 5mg of NaAs$_2$O$_3$ as electrolytic solution, keeping the sample as cathode and Pt as anode. On cathodic charging for one hour, a decrease in the intensity of the [0 0 2] peak of Ti$_3$Al is observed; upon further hydrogenation by cathodic charging, the peak intensity was found to increase. The same experiment was done at short intervals and it was found that the [0 0 2] peak disappears after 70 minutes of hydrogenation. On further
hydrogenation the peak intensity increases with respect to hydrogenation time up to 8 hours. Reproducability of the results was verified.

The initial decrease and the subsequent increase in the peak is explained based on the texturing taking place on hydride phase formation in Ti3Al. From the Rietveld refinement analysis it was found that the hydride phase has a the hexagonal structure with lattice parameters a=5.858 ±0.002 Å and c=4.657± 0.002 Å and a volume expansion of 2.13 % with respect to the parent phase. The lattice parameter ‘c’ did not change much due to hydrogenation whereas ‘a’ increased by 1.09 %. Further the hydride phase was found to be strongly oriented in [0 0 2] direction.

Both the intermetallic alloys Ti3Al and Ti2ZrAl were hydrogenated by gas phase charging method at 3.6 MPa for 8 days at room temperature. Ti3Al formed a hydride phase with the stoichiometry Ti3AlH4.76 whereas Ti2ZrAl formed Ti2ZrAlH4.96. In Ti3Al there are two hydride phases in the hydrided powder, one phase with cubic structure and the other with hexagonal structure. Rietveld refinement showed the presence of both the hydride phases in the sample. Differential scanning calorimetry measurement also confirmed the presence of two hydride phases in Ti3AlH4.76. The lattice parameter of the cubic hydride was found to be a= 4.366 Å. From XRD and DSC measurements it was found that the hexagonal hydride phase is more stable than the cubic hydride. In Ti2ZrAlH4.96 there was a partial amorphized phase, indicated by the rise in the background of the XRD pattern. Apart from the amorphous phase, the cubic and hexagonal hydrides of Ti3AlH peaks could be matched. Hence it forms a mixture of hydride phases. The combined XRD and DSC study in Ti2ZrAlH4.93 showed totally four phases viz. fcc hydride phase, hexagonal hydride phase, amorphous hydride phase and an un-identified phase. Thus the behavior of hydrogen in Ti3Al and Ti2ZrAl is found to be different when hydrogenation was done by the two methods discussed above.
Decomposition kinetic analysis was carried out on the DSC data and the activation energy was calculated. The area under the DSC endothermic peak was found and it fitted with many decomposition kinetic mechanism functions. From the kinetic analysis of the decomposition of hydrides, the decomposition mechanisms for both the hexagonal and cubic hydride phases were found to be matching with the Avrami-Erofeev function \([-\ln(1-\alpha)]^{1/4}\). The activation energies were calculated to be 379 kJ/mol and 52 kJ/mol for the hexagonal and cubic hydrides respectively.

The quantum mechanical description of electron states in Ti₃Al and its variation upon hydrogenation were computed using Linear Muffin Tin Orbital with Atomic Sphere Approximation (LMTO - ASA) method and the results are discussed. A brief theory about the LMTO method is given in Chapter V. Schwartz et al. have found that addition of hydrogen to Ti₃Al changed the structure of Ti₃Al to the cubic L1₂ structure. There are two octahedral sites in Ti₃Al with the L1₂ structure. One is at the body-centered site \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) coordinated by six-nearest neighbor Ti atoms, and the other is at the edge-centre \((\frac{1}{4}, 0, 0)\) position, coordinated by four Ti atoms and two Al atoms. Employing neutron scattering, Schwartz et al. found the stoichiometry of the hydride to be Ti₃AlH with hydrogen occupying the body-centered octahedral position. Using the LMTO-ASA, the total energy was calculated for hydrogen at the body centered octahedral site and edge centered octahedral site.

From the total energies the heat of formation of Ti₃AlH, was calculated and it is found that the value is close to that of the experimental value for Ti-H system. The partial DOS results show that the conduction band of Ti₃Al is drastically deformed when hydrogen is incorporated in the system. Hydrogen exhibits strong interaction with Ti atoms. Total energy studies confirm that the hydrogen prefers to occupy the body centered octahedral position.
Single-phase alloys of Ti\textsubscript{3}Al and Ti\textsubscript{2}ZrAl having DO\textsubscript{19} structure (hexagonal) were irradiated with 140 keV and 85 keV Ar\textsuperscript{+}, respectively. The irradiated samples were analysed using glancing angle incidence X-ray diffraction (GIXRD). There are no new peaks or amorphization signature in the GIXRD pattern of Ti\textsubscript{3}Al, irradiated by Ar\textsuperscript{+} up to a total dose of 1x10\textsuperscript{18} ions/cm\textsuperscript{2}. But in the GIXRD pattern of Ti\textsubscript{2}ZrAl irradiated by Ar\textsuperscript{+}, at the dose of 1x10\textsuperscript{17} ions/cm\textsuperscript{2} some new peaks appear with a rise in the background of the GIXRD pattern. Theoretical XRD pattern for cubic L1\textsubscript{2} phase was generated and the new peaks could be matched with the pattern. The un-irradiated and irradiated samples were analysed by Transmission Electron Microscopy (TEM). The sample irradiated up to a dose of 1x10\textsuperscript{17} ions/cm\textsuperscript{2} shows an amorphous ring with hexagonal phase. The sample, irradiated up to a dose of 5 x 10\textsuperscript{17} ions/cm\textsuperscript{2} shows cubic L1\textsubscript{2} phase along with amorphous ring. The stability of Ti\textsubscript{3}Al is explained based on the high mobility of point defects in Ti\textsubscript{3}Al, which presents rise of excess free energy on the defect cluster to reduce the free energy. Substitution of 25\% of Ti with Zr results in the formation of cubic L1\textsubscript{2} phase along with the partial amorphization presumably due to the defects or disordered zones produced in the collision cascades. Irradiation with Kr\textsuperscript{+}, which introduces much higher collision cascades, produces complete amorphization.

**SCOPE FOR FUTURE WORK**

In this study considerable work has been carried out on Ti\textsubscript{3}Al and Ti\textsubscript{2}ZrAl system. Ti and Zr belong to the same group (IV). This studies indicate that the substitution of Zr does not change the unit cell structure, where Zr occupies the same position of Ti in the space group P6\textsubscript{3}mmc, with different occupancy. Formation of hydride phase upon hydrogenation by various techniques has been studied which brought out different hydride phases produced by different hydrogenation methods. On gas phase charging Ti\textsubscript{2}ZrAl produces both cubic and hexagonal hydrides. Hydrogen position in Ti\textsubscript{3}AlH\textsubscript{4} is not known. It will be interesting to determine positions of H by neutron diffraction or channeling.
studies. Mori et al hydrogenated Ti$_2$ZrAl at 5 MPa and the sample became completely amorphous, whereas in this study hydrogenation done at 3.6 MPa and it produced only partial amorphization. It will be interesting to investigate the amorphization behaviour of alloys with different composition Ti$_{2-x}$Zr$_x$Al with x ranging 0 to 2.5 as a function of pressure and then the decomposition kinetics.

Ti$_2$ZrAl was rendered amorphization by hydrogen gas charging method which produces only chemical disorder. Ion irradiation on Ti$_2$ZrAl showed a dependence on projectile mass. Ar$^+$ irradiation produced partial amorphization along with cubic L1$_2$ phase whereas Kr$^+$ irradiation produces complete amorphization. This aspects needs further investigation in order to study the effect of projectile particle mass as well as the irradiation temperature on the amorphization behaviour of Ti$_2$ZrAl.

Ti$_3$Al could not be rendered amorphous by Ar$^+$ irradiation at room temperature, it will be interesting to study the amorphization behaviour of Ti$_3$Al at low temperatures. 25 % substitution of Ti by Zr could make the compound amorphous, which establishes the role of Zr in the amorphization process. However its exact role whether it reduces point defect mobility reduces the critical density of defect for amorphization could not be identified. This needs further investigation on alloys having different composition i.e Ti$_{3-x}$Zr$_x$Al alloy with x ranging from 0 to 2.5.