Chapter 8

Conclusion

In this chapter we summarize all the findings in the previous chapters and conclude. We also indicate some of the areas where future work can be continued.

8.1 Conclusion

We have investigated in the present thesis the effect that the Al replacement has on the Ni-Mn-Z (Z is Sn, Sb and In) class of ferromagnetic shape memory alloys. We prepared alloys with composition of $Ni_2Mn_{1.36}Z_{0.64-x}Al_x$, where x was varied from 0.24 to 0.40 in step of 0.04 depending on Z. Our aim was to develop a system intermediate to pure Z and Al based systems so that the resultant system had the better functional capabilities.

We prepared our samples using a tri-arc melting furnace and they were characterized using various techniques as mentioned in the Chapter 2. The X-ray diffraction patterns showed that the replacement of Al with Z lead to stabilization of $L2_1$ phase in the system. All samples showed martensitic transformations thus showing that Al replacement did not suppress it. It was further found that the replacement shifted the MT temperature towards room temperature. The substitution was found to affect the magnetism differently in various systems. In the Sn based system the magnetism of the austenitic phase fell as the Al content was increased and was also found that with increase in the Al, the undesirable B2 phase in the system increased.

The functional properties of the system like magnetocaloric effect, magnetoresistance and exchange bias effect were studied in the Chapter 4. The MCE effect was measured in a field of 1.5 T. The replacement of Al by the Sn was found to enhance the MCE in the sample to almost twice of that of the pure Sn system. We also showed that the measurement of ΔS_M using an indirect method of magnetization measurement agreed with more direct method of calorimetric measurements in our samples, so showing that there was no over-estimation of the ΔS_M. The Sb replacement system did not display the large inverse MCE as observed in Sn replaced system but nevertheless the conventional MCE observed in the former system was found to have better RC values then the Sn based system. The system also displayed the EB effect which may find application in future spintronic devices. Thus overall the Al replacement in the system enhanced the functional capabilities of the system.

The dynamics of the low temperature martensitic phase was studied in the Chapter 5, using both ac and dc magnetization measurement techniques. The linear ac susceptibility measurements showed that the system most probably froze in the spin glass state and the

frozen entities were magnetic clusters rather than individual spins. It was also observed that the cluster size showed dependence on the concentration of Al for Sn based system, decreasing with increase in Al content. The nonlinear third harmonic measurements in the Sb and In based systems did not show the typical signature of the spin glass. Thus the freezing in the systems most probably came from progressive blocking of the magnetic clusters rather than due to spin glass.

The dynamical study with dc magnetization in Sn and Sb based system showed similar behavior where the (H, T) phase diagram of the system broke down above internal exchange bias field. It was found that above and below the breakdown the system had different dynamics. The Sn based system was found to unfreeze along the transverse line in the low field below the breakdown point whereas the In based system did not display any such behavior even at higher field and the cluster in these cases relaxed along the longitudinal line.

The magnetocaloric effect was found to decrease as the Al content increased in the Sn based system. To enhance the MCE we performed low and high temperature secondary heat treatments on $Ni_2Mn_{1.36}Sn_{0.32}Al_{0.32}$ and $Ni_2Mn_{1.36}Sn_{0.28}Al_{0.36}$ respectively. It is reported in the Chapter 6. While the low temperature annealing in $Ni_2Mn_{1.36}Sn_{0.32}Al_{0.32}$ decreased the peak value of entropy change, the refrigerant capacity of the sample was found to increase as compared to quenched sample. Frequency dependent susceptibility showed that samples underwent freezing at low temperature and the sizes of the magnetic clusters increased as the annealing temperatures were increased. The frequency dependence of χ_3 further showed that the dependency most probably came from the random freezing of clusters without frustration. The high temperature heat treatment on the other hand of $Ni_2Mn_{1.36}Sn_{0.28}Al_{0.36}$, increased the MCE in the sample almost two times of that of quenched samples. The effects arising due to secondary heat treatments were reported to occur due to increase in the ordering in the sample. It was thus shown that the better functional properties can be obtained even at higher concentration of Al in Sn based system.

We have compared the nature of structural transformation, magnetism, magnetocaloric effect and magnetoresistance for the samples with composition of $Ni_2Mn_{1.36}Sn_{0.40}Al_{0.24}$

and $Ni_2Mn_{1.36}Sb_{0.40}Al_{0.24}$ in Chapter 7. We have shown the effect a *sp* element can have on the magnetism and properties like MCE and MR. The presence of Sb weakened the AFM interaction in sample leading to increase in magnetism of both austenitic and martensitic phase. This effect being more pronounced in martensitic phase, led to decrease in magnitude of ΔM, MCE and MR by more than an order of magnitude.

Thus we found that Al replacement in Ni-Mn-Z based system gave a system which has better properties than the parent system. The Al replacement provided a cheaper alternative to the costly Z elements (Sn, Sb and In). The properties of systems and there transformation temperatures can be easily controlled by changing Al content and also by giving proper heat treatment. Thus overall we get systems which have superior properties to Ni-Mn-Al system. The dynamic studies offer us insight into the possible origin of magnetism in Ni-Mn-Z systems and further showed that freezing in the system in martensitic phase was mostly outcome of progressive blocking of the magnetic cluster and not of spin glass nature.

8.2 Future scope

In our investigations we measured mostly the dynamics and functional properties of the systems prepared. The effect of substitution of Al on the mechanical property of the system could not be studied for the lack of the facilities and time. Further the substitution was only carried out in the $Ni_2Mn_{1.36}Z_{0.64}$ alloy with Z as Sn, Sb and In. While the substitution in Sn and Sb system gave systematic and desirable results, the properties of In system was inferior owing to structural transition taking place above the magnetic transition. Thus different composition of In system may be tried for substitution of Al to achieve better functional properties in them.