Chapter 7

Overall conclusions and future prospects

7.1 Overall conclusions

- The phase of interest, LTP MnBi was synthesized using vacuum-arc melting and confirmed through XRD, DSC and TEM studies. However, the presence of Mn and Bi phases due to incomplete peritectic reaction were also observed.
- The as-cast alloy displayed low coercivity values (~570 Oe), however, it was improved up to 7.5 kOe after 8 h of room-temperature high energy ball milling. Nonetheless, the desired LTP decomposes upon milling for more than 2 h.
- In addition, the milled samples also displayed asymmetric M *vs.* H loops. This was attributed to “Spontaneous Exchange Bias” phenomenon. Hitherto never reported in Mn-Bi system, a considerable exchange bias field (H_{EB}) of 1200 Oe was observed at room temperature. This feature opens the possibility of Mn-Bi system’s applicability in spin-valve and magnetic recording devices.
- Despite an enhancement in H_C values and the display of exchange bias phenomenon, reduction in M_S values was observed for milled samples. Oxidation due to localized heating, LTP decomposition due to induced lattice strain and the anti-site disorders of Mn were the three major reasons to cause reduction in the M_S values.
- Using a simple two-step, solvothermal technique followed by calcination at 700 °C, single phase Fe_3C@C and FeNi@C nanoparticles were successfully synthesized. This was confirmed using the XRD and TEM measurements. The Fe_3C@C nanoparticles displayed an impressive saturation magnetization ~150 emu/g, whereas its M_r and H_C values were 4.35 emu/g and 79 Oe respectively. The HAADF measurements displayed a carbon coating of average 5 nm thickness around the Fe_3C

particles. The FeNi@C nanoparticles showed a M_S value of 147 emu/g, M_r ~ 3.4 emu/g and H_C~ 14 Oe.

- Further, Co@C nanoparticles with H_C~ 470 Oe and a M_S value of 140 emu/g were also prepared employing the sol-gel technique followed by calcination at 700 °C. This was corroborated using the XRD and TEM measurements. The nature of carbon coating of all the three soft magnetic phases (Fe_3C@C, FeNi@C and Co@C) was confirmed to be reduced graphene oxide (r-GO) with the help of Raman Spectroscopy.
- Consequently, nanocomposites prepared with the hard phase (MnBi) and the soft phases (e.g. Fe_3C@C or FeNi@C or Co@C) using cryo-milling technique helped in addressing the lacuna found during the room-temperature milling. Due to the sub-zero temperatures employed during cryogenic milling, relatively lower lattice strain values than room-temperature milling were observed. This led to a comparatively lesser LTP decomposition and negligible oxidation issues as reflected in the M_S values of the cryo-milled samples.
- Among the synthesized nanocomposites of $Mn_{55}Bi_{45}$ and soft phases (e.g. Fe_3C@C or FeNi@C or Co@C) of varying proportions (5, 10, 15, and 20 wt.%), the $Mn_{55}Bi_{45}$/Co@C composite displayed the best properties. It achieved a H_C value of 10.9 kOe, M_S ~ 67.5 emu/g and M_r ~40.3 emu/g for $Mn_{55}Bi_{45}$ +15 wt.% Co@C. In contrast, the pure cryo-milled $Mn_{55}Bi_{45}$ powder displayed a M_S value of 40.9 emu/g whereas M_r and H_C values were around 20.9 emu/g and 6.7 kOe respectively.

Table 7.1. Comparison of the best magnetic properties obtained among the three nanocomposite systems.

S.No	System	M_S(emu/g)	M_r(emu/g)	H_C (kOe)
1.	$Mn_{55}Bi_{45}$ (pure)	40.9	20.9	6.7 kOe
2.	$(Mn_{55}Bi_{45})_{100-x}$/(Fe_3C@C)$_x$ (x=10 wt.%)	57	35	6.6
3.	$(Mn_{55}Bi_{45})_{100-x}$/(FeNi@C)$_x$ (x=15 wt.%)	63	38	7.9
4.	$(Mn_{55}Bi_{45})_{100-x}$/(Co)$_x$ (x=15 wt.%)	67.5	40.3	10.9 kOe

➢ This study also suggests that phases such as Fe_3C@C, FeNi@C and Co@C can be used as soft magnetic phases in the preparation of exchange spring magnets. The carbon coating over the nanoparticles helped in improving their oxidation resistance and facilitated the exchange coupling the hard and soft phases through spin tunneling.

7.2. Future prospects

a. Since, LTP has attractive magnetic properties at elevated temperatures. The high-temperature magnetic studies up to 670 K, on the prepared exchange-spring composites can be performed for better understanding.

b. As the recommended cryogenic ball milling results in isotropic powders of exchange spring nano-composites, magnetic field compaction can be done further to induce anisotropy. It would be interesting to observe the combinatorial magnetic behaviour of the soft and hard phases of the composite during alignment under an external magnetic field.

c. Another challenge that needs to be addressed is the preparation of bulk magnets from the milled composite powders. Comparative studies can be carried out between the conventional spark plasma sintering and the less explored microwave sintering techniques for the densification of the composites. Further, understanding the effect of microwave sintering and its parameters on the overall magnetic properties of the prepared systems.

d. Exploration and establishment of process techniques for other soft magnetic phases including the conventionally used α-Fe and $Fe_{65}Co_{35}$ with carbon coating for preparing exchange spring magnets may be studied.

e. The developed soft phases i.e., Fe_3C@C, FeNi@C and Co@C can be used in the preparation of exchange-spring magnets with commercially available permanent magnets like the Nd-based and Sm-based to improve their magnetic performance.