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Effect of rapid quenching on the magnetic and structural properties of Bi–MnBi composites

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Rapid quenching of hypereutectic Bi–Mn alloys with compositions ranging from Bi–1.5 wt% Mn (Bi–5 at% Mn) to Bi–20 wt% Mn (Bi–50 at% Mn) was carried out to achieve an optimum constitution of the ferromagnetic MnBi phase. Microstructural investigations by optical and electron microscopy techniques revealed the presence of very fine MnBi particles in the as-spun samples. The results of the microstructural and thermal analysis studies have indicated that it is possible to achieve control over the size and amount of the ferromagnetic phase by melt spinning. Some initial results of magnetic properties of melt-spun ribbons are also presented.

1. Introduction

Among the various manganese alloys with ferromagnetic phases, the intermetallic compound MnBi is of particular interest as a hard magnetic material because of its very high anisotropy and magneto-optic properties [1–3]. In recent years eutectic Bi/MnBi composites, unidirectionally solidified under 1-g and low-g conditions, have been extensively studied [4–8]. These studies have achieved MnBi rods of reduced diameters with enhanced magnetic properties. However, a natural limitation at the eutectic composition is that the volume fraction of the potentially useful ferromagnetic MnBi phase is small (3.2% by volume) [9].

At hypereutectic compositions, because of the difference in densities and in melting points of the components, manganese separates as a primary constituent and rises to the top of the melt during solidification. This prevents the manganese from being available for the peritectic reaction at 719 K, leading to severe macrosegregation [10]. However, several attempts have been made to produce pure MnBi by other techniques such as thin film vapour deposition followed by annealing [1, 11, 12], sintering of pure bismuth and manganese powders [2] and even crystal pulling [13, 14]. For applications employing MnBi as a high density magneto-optical recording medium, a crystallite size as large as several microns is considered to be too large [15], a micron being optimal.

In the present work, the effect of rapid solidification on the size and amount of the ferromagnetic phase in hypereutectic Bi–Mn alloys have been investigated. Rapid solidification brings about supersaturation along with the elimination of macrosegregation. The results on the comparative study of the microstructural features of as-spun ribbons and magnetically annealed ribbons are presented. Thermal analysis studies of melt-spun ribbons as well as the as-cast Bi–Mn alloys are also presented. The effect of melt spinning on the magnetic properties of Bi–Mn alloys is discussed. The results of X-ray diffraction studies on melt-spun ribbons are reported elsewhere [16].

2. Experimental procedure

Hypereutectic alloys with compositions ranging from Bi–1.5 wt % Mn to Bi–20.8 wt % Mn were prepared from 99.999% Bi and 99.99% Mn. For preparation, the weighed components were sealed in a quartz tube under a partial pressure of argon and melted in the induction furnace. The resulting alloys were then melted and then directed on to a copper drum of 10 cm diameter, rotating at 4000 r.p.m. Ribbons of 25 to 50 μm thick, 3 to 4 mm wide and up to 60 mm long were obtained.

The microstructures of the as-cast and as-spun ribbons were investigated using optical, scanning and transmission electron microscopy techniques. Thermal analysis studies were carried out using a differential scanning calorimeter, Perkin–Elmer DSC-2C.

The as-spun ribbons were sealed in pyrex tubes under a partial pressure of argon and annealed at 523 K in a magnetic field of 5 kG for 10 h. The applied magnetic field was perpendicular to the long-axis of the ribbons. Initial magnetization measurements were carried out at Grumman Aerospace Corporation, New York [17], using a vibration sample magnetometer. The samples were subjected to magnetizing fields up to 10 kG at room temperature.

3. Results and discussion

3.1. Microstructural studies

The optical micrograph in Fig. 1 shows the typical microstructure of an as-cast ingot of the Bi–20.8 wt % Mn alloy. The ferromagnetic MnBi phase (grey) is observed along with the undissolved manganese particles (black) embedded in a diamagnetic bismuth-rich (white) matrix. Fig. 2 is an optical micrograph of the refined microstructure of the same alloy after rapid solidification, in the longitudinal section of the ribbon. The lower section is the chill surface. A gradual increase in the size of the MnBi crystallites away from the chill surface is due to the gradual decrease in the cooling rate away from the drum contact side.

The micrograph shown in Fig. 3 corresponds to a

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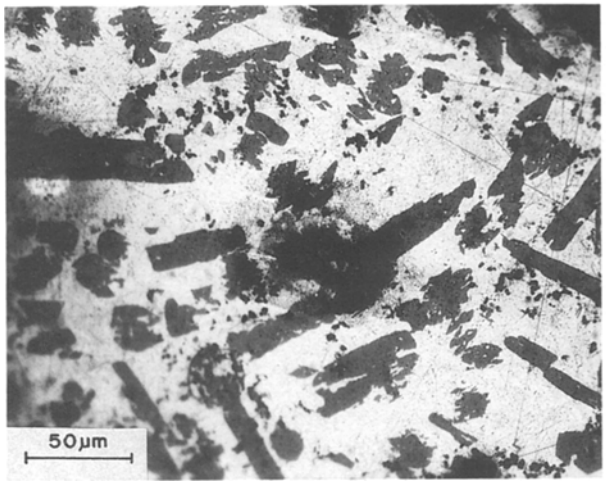

Figure 1 Optical micrograph of as-cast Bi–20.8 wt % Mn alloy.

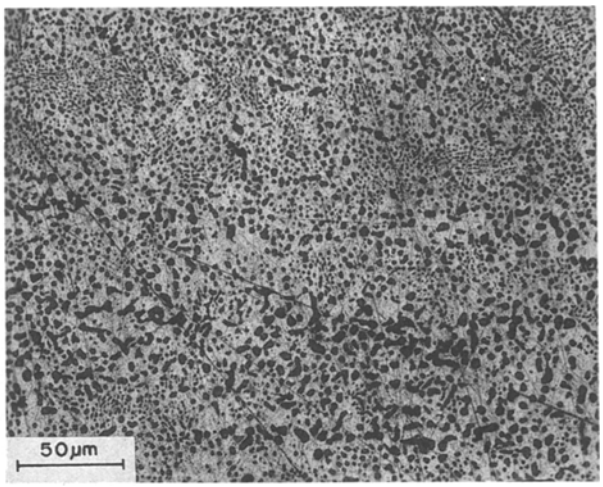

Figure 3 Optical micrograph of magnetically annealed Bi–6 wt % Mn ribbon (transverse section).

magnetically annealed ribbon of melt-spun Bi–6 wt % Mn alloy (transverse section). This consists of MnBi particles ranging from 2 μm to 10 μm in size. Coarsening is observed as the Mn concentration increases. This is shown in micrographs (Figs 4 and 5) for a Bi–20.8 wt % Mn field treated ribbon, with MnBi particles ranging from 2 μm to 18 μm. Comparison of Fig. 2 with Fig. 5 clearly shows a significant coarsening effect as a result of magnetic annealing for Bi–20.8 wt % Mn ribbons. It is interesting to note that the MnBi phase exhibits a primarily dendritic morphology in some regions of the ribbon (Fig. 5). A similar observation has been reported previously [18], with no detailed comments.

Fig. 6 shows the scanning electron micrograph (backscattered image) of a Bi–20.8 wt % Mn melt-spun ribbon, using the atomic number (compositional) contrast (At. no. of Bi: 83; At. no. of Mn: 25). The average composition of the sample was found to be Bi–20.8 wt % Mn (or Bi–50 at % Mn) from energy dispersive spectroscopy (EDS) analysis. The EDS analysis of the black regions revealed the equiatomic concentrations of Bi and Mn, confirming that the regions are the MnBi phase.

Transmission electron microscopy (TEM) investigations revealed the presence of a cellular structure, which is a commonly observed morphology in rapidly solidified materials. As shown in Fig. 7, for a Bi–6 wt % Mn melt-spun alloy, the cell size is in the order of 0.3 to 0.5 μm. The TEM studies on Bi–3 wt % Mn melt-spun alloys showed very fine precipitates of 0.02 μm in size, as seen in Fig. 8. The ribbons which were electron-transparent after melt-spinning were chosen for the above study. Unidirectional studies [6, 19] have shown that the coercivity of MnBi increases with reduction in rod diameter. Hence very fine precipitates of 0.02 μm size in the current study are expected to have a much higher coercivity value. Some of the magnetic properties of these ribbons are discussed below.

3.2. Magnetic property studies

The hysteresis curves obtained at room temperature for three melt-spun samples are shown in Fig. 9. None of the samples have saturated at 10 kG, indicating a strong paramagnetic component in the samples. This is in contrast to thin films, which have been found to saturate always in the neighbourhood of 3.75 kG irrespective of the film thickness [20]. Apart from the two equilibrium phases–MnBi (referred to as Low

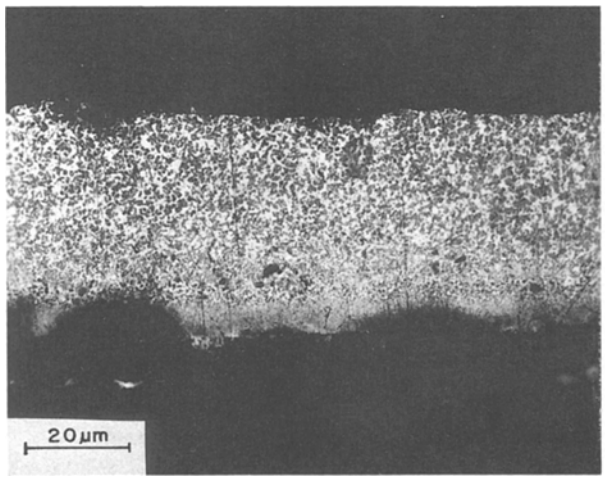

Figure 2 Optical micrograph of as-spun Bi–20.8 wt % Mn alloy (longitudinal section).

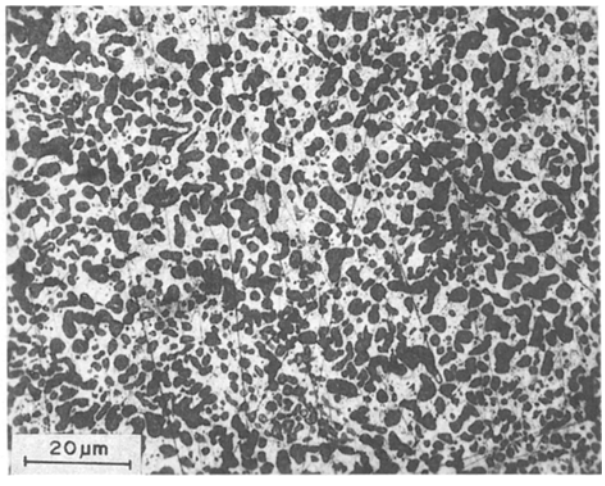

Figure 4 Optical micrograph of magnetically annealed Bi–20.8 wt % Mn ribbon (transverse section).

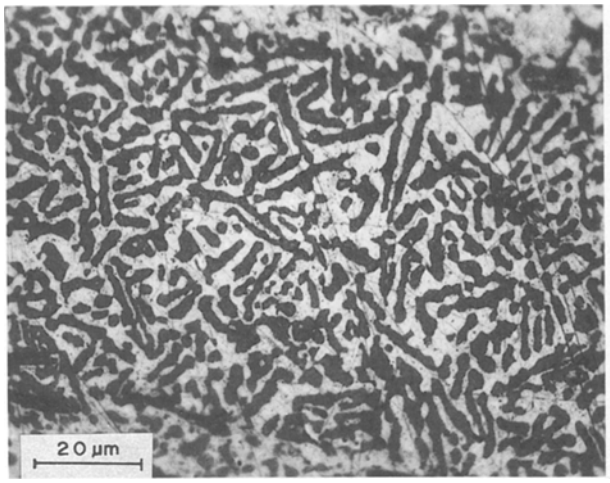

Figure 5 Optical micrograph of magnetically annealed Bi–20.8 wt % Mn ribbon different region from that of Fig. 4).

Temperature Phase or LTP) and $Mn_{1.08}$ Bi (referred to as Quenched High Temperature Phase or QHTP), samples processed by directional solidification have been observed [19] to consist of another magnetic phase. This phase, termed the high coercivity or HC phase, is a metastable phase found to coexist with the LTP phase and is paramagnetic at room temperature. The HC phase is paramagnetic at room temperature, but transforms to the ferromagnetic state between 295 and 77 K [19], whereas, QHTP is ferromagnetic at room temperature with a Curie temperature of 440 K [21]. The authors are of the opinion that in the melt-spun samples the strong paramagnetic component present is the HC phase. Further magnetic measurements at low temperatures, currently in progress, will determine the amount of the paramagnetic component in these melt-spun ribbons.

The annealed samples have extremely weak signals, which might be a consequence of an insufficient quantity of the sample used during measurements. (The hysteresis curves shown in Figs. 9b and 9c have been optimised for clarity.) This may also be a consequence of contamination during heat treatment of the samples [17]. In addition, the HC phase is known to transform to the LTP phase with heat treatment [19].

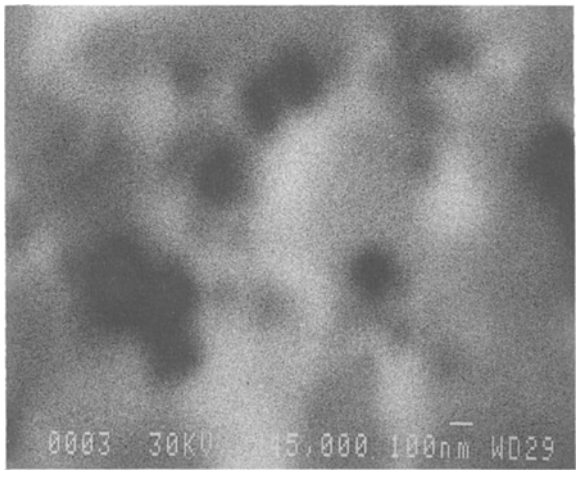

Figure 6 Scanning electron micrograph of as-spun Bi–20.8 wt % Mn alloy.

Figure 7 Transmission electron micrograph of as-spun Bi–6 wt % Mn alloy.

Hence one can expect an increase in the room temperature magnetisation and intrinsic coercivity for annealed samples. In the current study the magnetisation is lowered by about an order of magnitude and the coercivity is very slightly increased. Also, the coercivity of the annealed Bi–6 wt % Mn sample is approximately 50% greater than that of the Bi–20.8 wt % Mn sample. This is due to a decreased MnBi particle size in the sample with lower manganese content, as confirmed by our microstructural investigations. X-ray analysis has indicated that the QHTP phase completely transforms to the LTP phase when the melt-spun ribbons are annealed for 15 h and more.

Coercivity is known to be dependent on various factors such as internal stresses, saturation magnetisation and crystalline anisotropy [22]. In MnBi thin films, even the method of preparation of the film has been found to have a great effect on coercivity [22]. However, it is important to note that an increase in coercivity is much easier to attain by influencing the size and aspect ratio of the particles rather than by

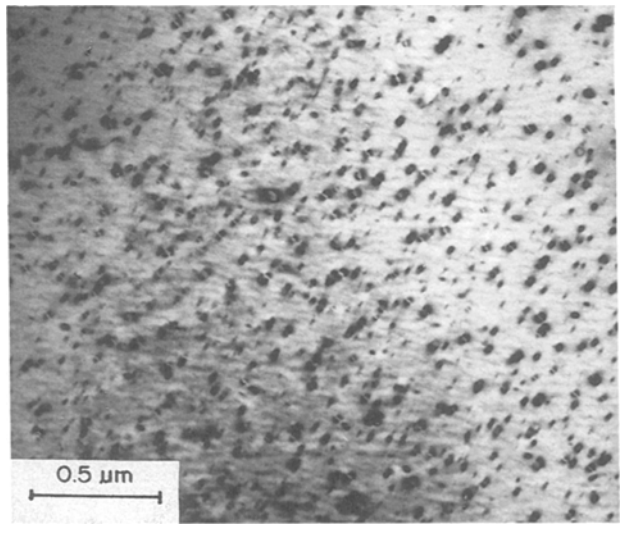

Figure 8 Transmission electron micrograph of as-spun Bi–3 wt % Mn alloy.

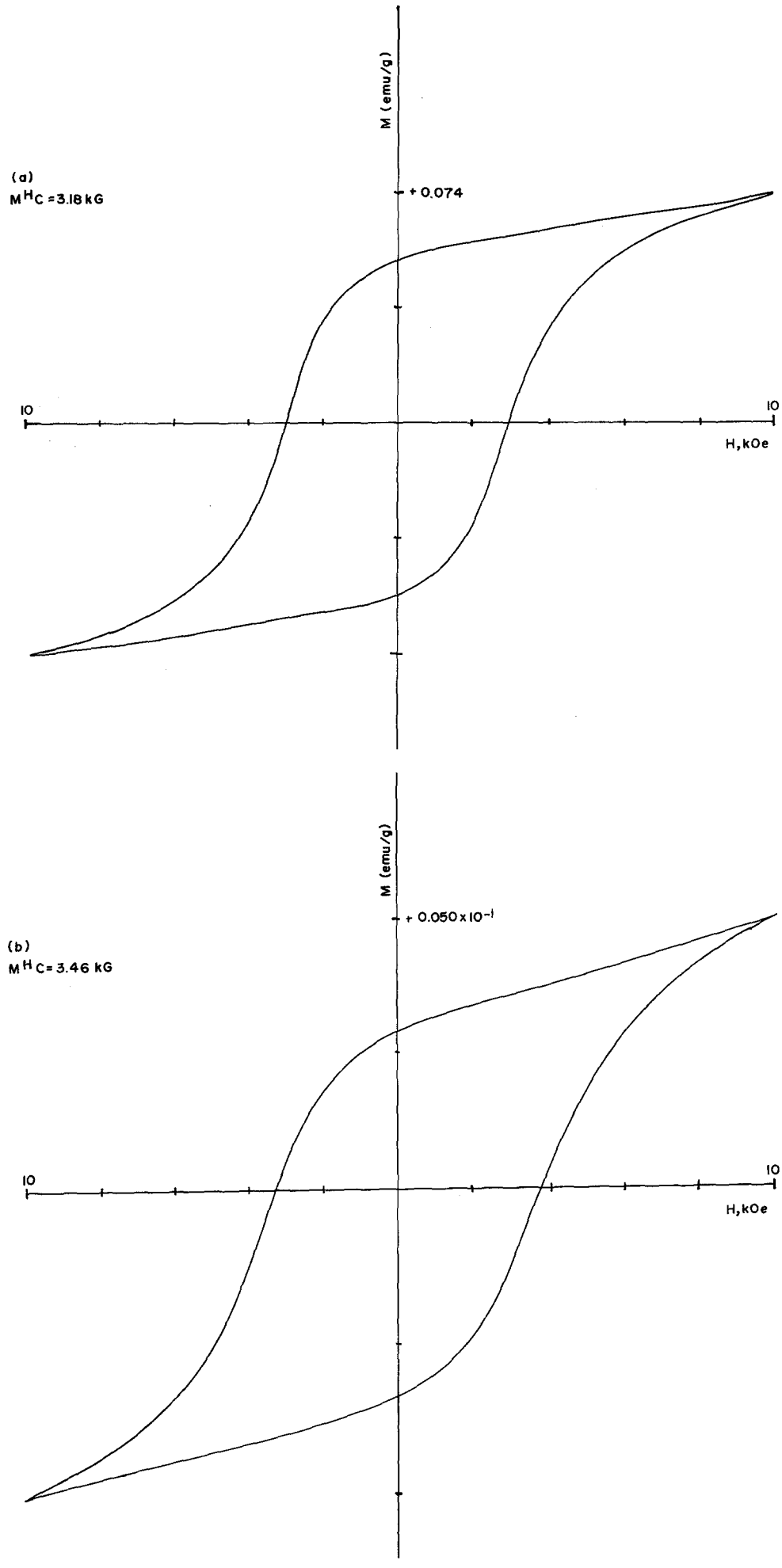

Figure 9 Room temperature hysteresis curves of (a) as-spun Bi–20.8 wt % Mn ribbons, (b) magnetically annealed Bi–20.8 wt % Mn ribbons, and (c) magnetically annealed Bi–6 wt % Mn ribbons.

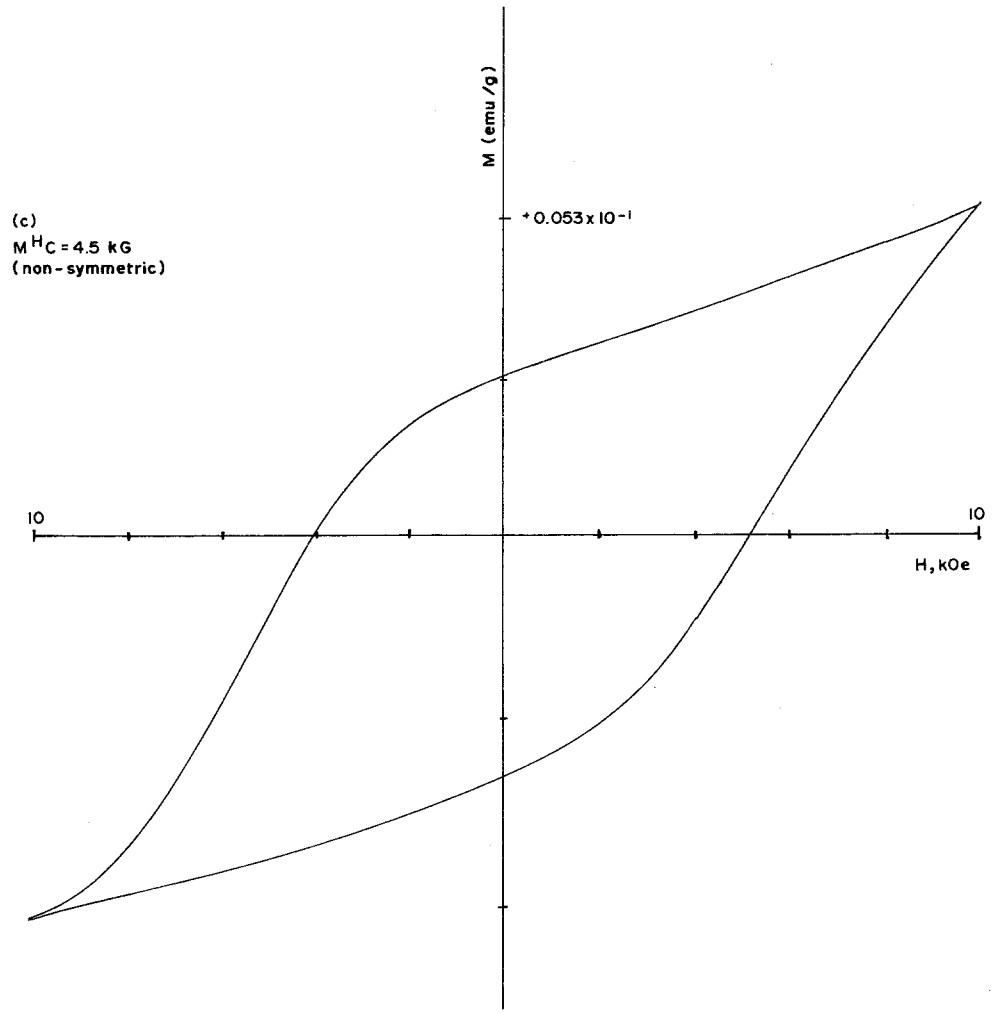

Figure 9 Continued.

applying a stress [23]. This leads us to conclude that by proper control of the size and shape of the MnBi particles in the rapidly solidified ribbons it is possible to obtain the required magnetic properties for potential applications.

3.3. Thermal analysis studies

The thermal analyses of several samples were carried out at a heating rate of 20 deg min^{-1} using a differential scanning calorimeter(DSC) and the results are shown in Fig. 10. The heating curves show a

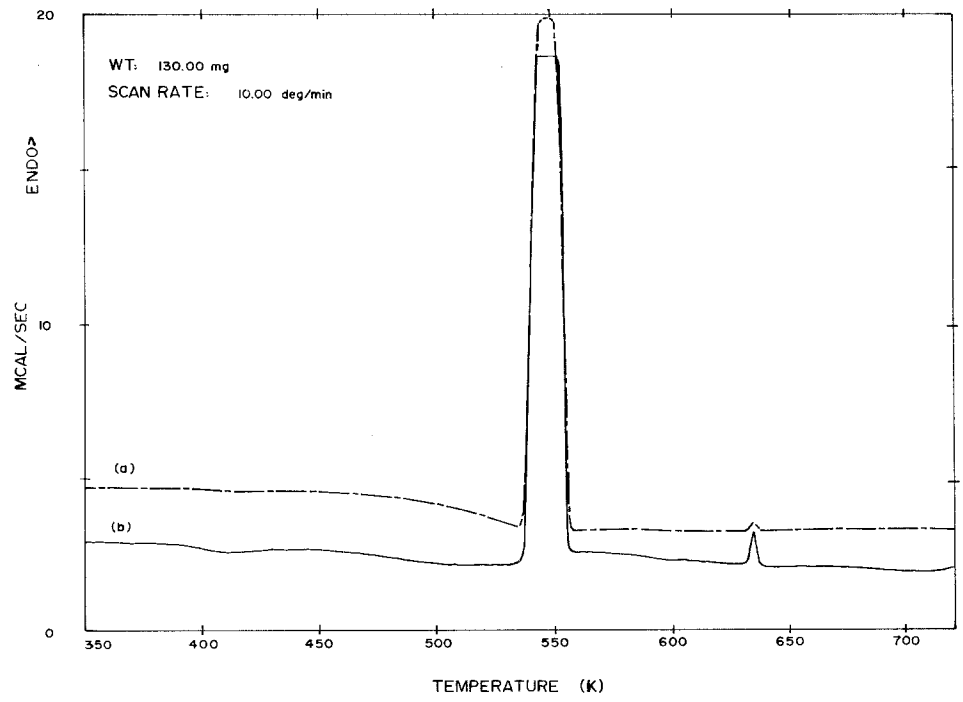

Figure 10 DSC curves for melt-spun (a) Bi–1.5 wt % Mn, and (b) Bi–3 wt % Mn alloys.

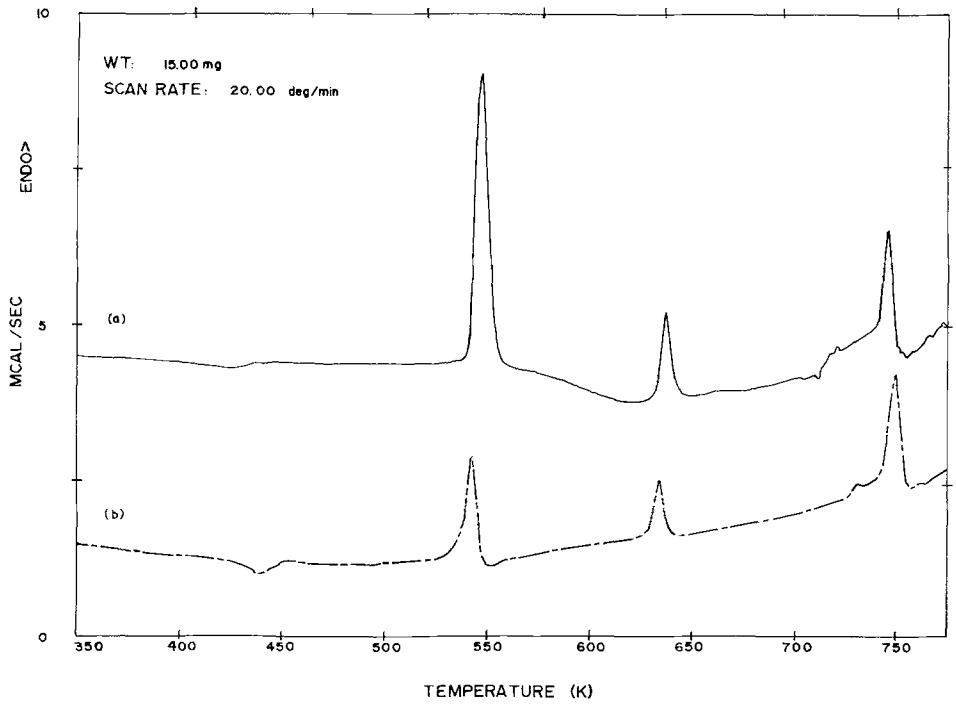

Figure 11 DSC curves for melt-spun (a) Bi–9 wt % Mn, and (b) Bi–20.8 wt % Mn alloys.

precipitation reaction to occur in the range 393–433 K for all the compositions studied. Investigations of the kinetics of formation of MnBi thin films [24] have shown that formation of the MnBi phase begins at about 433–453 K. The most common method used to prepare MnBi thin films is to deposit a layer of manganese on the top of a layer of bismuth by vacuum evaporation, followed by annealing [25] between 373 to 473 K. As the annealing proceeds, more Mn atoms are believed to diffuse into appropriate bismuth (interstitial) lattice sites to form MnBi [26]. In the melt-spun ribbons during precipitation in the range 393–433 K, we presume excess manganese from the supersaturated solid solution as well as the QHTP phase ($Mn_{1.08}$ Bi) diffuses out to form more MnBi (LTP). Also, it is anticipated that the migration rate of Mn will have increased considerably due to vacancy excess so as to form MnBi even at lower temperature as compared with vapour deposited thin films. It is also noted that as the manganese content in the alloy has increased, the amount of precipitated MnBi phase has increased as expected (Fig. 11). This may be deduced from the plots that show the area of the exothermic peak when the same amount of sample is used for the DSC runs.

A comparison of the heating curves for the as-cast (Fig. 12a) and the as-spun samples (Fig. 12b) of Bi–20.8 wt % Mn alloy shows clearly that more manganese has precipitated out in the case of rapidly solidified ribbons. This suggests that the melt-spinning has been a successful technique to increase the solid solubility of manganese in bismuth in Bi–Mn system. In addition, X-ray diffraction studies have indicated the retention of QHTP phase at room temperature in the as-spun ribbons [16]. Together with the results from the present microstructural studies it is apparent that melt-spinning permits the control of both the amount and size of the ferromagnetic phase.

In addition, the DSC curves indicate three transformations, at temperatures 533 K, 628 K and 719 K, respectively, in accordance with the following known reactions from the phase diagram [27]:

$$\text{At } 533\,\text{K: Bi} + \text{MnBi} \rightarrow \text{Liq}$$

$$\text{At } 628\,\text{K: MnBi} \rightarrow Mn_{1.08}\,\text{Bi} + \text{Bi-liq}$$

$$\text{At } 719\,\text{K: } Mn_{1.08}\,\text{Bi} \rightarrow \text{Mn} + \text{Bi-liq}$$

In general, ferromagnetic to *para*magnetic changes are known to be second order transitions [28]. But the magneto-structural transition of the MnBi phase at 663 K from the ferromagnetic to the *para*magnetic state has been reported to be a first order process by Roberts [29], and others [30]. In this study, the transition at the Curie temperature (633 K) could be detected (Fig. 10) for low concentrations of manganese (up to 3 wt % Mn). From the type of peak observed at the Curie temperature it can be inferred that the transition is of the first order kind. At higher concentrations of manganese, the magneto-structural transition overlaps with the transformation reaction at 628 K.

4. Conclusions

Hypereutectic alloys of Bi–Mn with composition Bi–1.5 wt % Mn and Bi–20.8 wt % Mn were successfully melt-spun; some refinement of the microstructure and cellular morphology were observed in the as-spun ribbons and are associated with the effects of rapid quenching. Optical and electron microscopy techniques revealed very fine MnBi particles in dilute alloys. As the manganese content increased the size of the MnBi phase also increased.

The MnBi was found to precipitate from the as-spun ribbons upon heating in the temperature range of 393 and 433 K. DSC studies have shown that through melt-spinning it is possible to achieve a supersaturation of Mn in Bi. Magnetic property measurements at room temperature have indicated the presence of a *para*magnetic component in the ribbons, which is

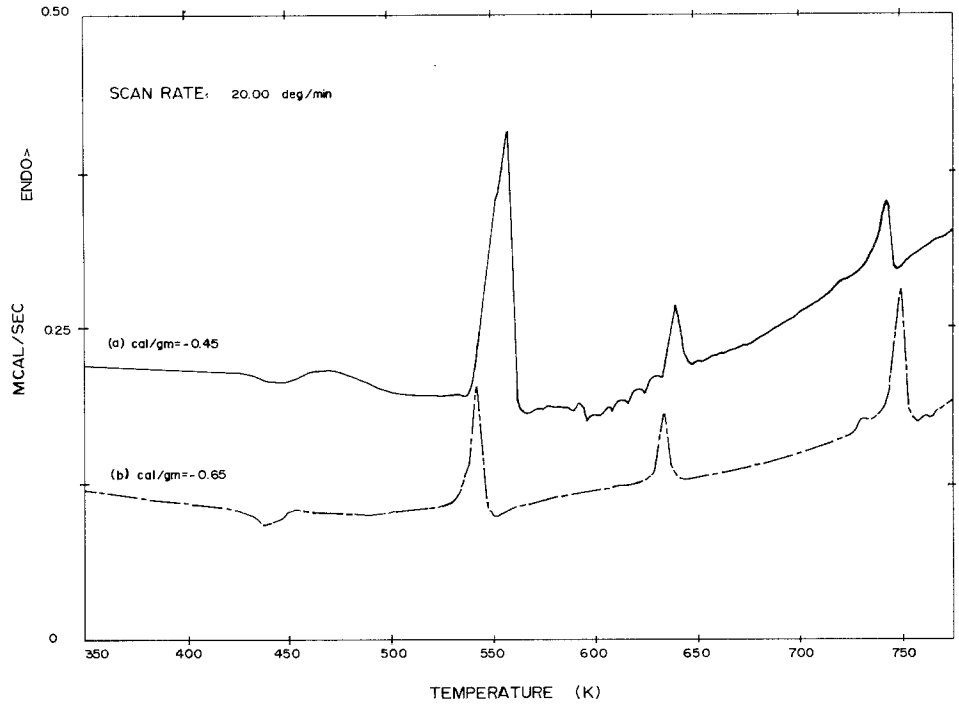

Figure 12 Normalised DSC curves for Bi–20.8 wt % Mn (a) as-cast, and (b) as-spun alloys.

believed to be the high coercive phase as reported in unidirectional solidification studies.

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