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FORMATION OF MnBi BY MECHANICAL ALLOYING

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In this report we demonstrate that mechanical alloying is an alternative process to produce the intermetallic compound MnBi. Magnetically MnBi powder is prepared from the elemental powders by mechanical alloying in a planetary ball mill and then solid-state reaction at a relatively low temperature. The MnBi powder was aligned in a magnetic field and isostatic pressed. The X-ray pattern of powder reacted clearly shows the intensity peaks of the MnBi phase. After annealing the magnetization was about 1.0×10^{-4}T m^3/kg.

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1. Introduction

Many authors have investigated the magnetic properties of the phase in the Mn–Bi systems. As can be seen from the phase diagram [1] the phase cannot be prepared directly from a melt of the desired composition. Instead, they are prepared by low-temperature diffusion of elemental powders, or by vapor deposition techniques or by controlled growth of a solid from a Bi rich melt.

After Notis et al. [2] an alloy containing about 2 at% Mn and 98 at% Bi should solidify at 503 K to give an eutectic constant of about 3 vol% ferromagnetic MnBi in a matrix of diamagnetic Bi.

Whereas in conventional alloying the mixing of the elements takes place in the melt and the solid alloy is formed by solidification, mechanical alloying uses an interdiffusional reaction [3], which is possible due to the formation of ultrafine layered composite particles during the milling process in a ball mill.

Several authors have reported amorphization during ball-milling of powder mixtures of immiscible elements. Amorphization by ball-milling, of elemental mixtures with positive heat of mixing ($\Delta H_{\text{mix}} > 0$) has been attributed to the increase in the free energy of the elemental powders due to a very high defect density generated by repeated low-temperature deformation. It has been suggested that this energy is mainly stored in a large grain boundary density (as a nanocrystalline structure emerges from the dislocation cell structures of heavily sheared zones).

The metal powder particles are trapped by the colliding balls, heavily deformed and cold welded leading to characteristically layered particles. Depending on the thermodynamics of the alloy system, on the mechanical workability of the starting powders and on the milling conditions, the interdiffusional reaction to form the alloy can either take place during the milling or during a following heat treatment.

2. Experimental

The starting materials for this study were 99.9% pure Mn and Bi powders of particle size 45 μm. The powders were mechanically alloyed in a high energy mill (Fritsch "Pulverisette 5") under an argon atmosphere for 120 h. The powders were alignment in a magnetic field of 1.6 T parallel to the cylindrical axis and isostatic pressed under a pressure of 500 MPa. A pressed sample was heated in atmosphere of argon at 533 K for 20 minutes. The samples were cylindrical 3.2 mm in diameter and 6.3 mm in length. The density of specimens varied from 6.6 to 6.7 g/cm^3. The crystal structures of the samples were determined by X-ray diffraction with Cr K_α radiation. Magnetization measurements were carried out in the temperature range from 300 K to 700 K and in an applied magnetic field up to 9.5×10^5 A/m using a Faraday balance. The virtual Curie point, was obtained by extrapolating the σ vs. T. The initial susceptibility was measured in an alternating field of 40 A/m at 100 Hz by means of a bridge of mutual inductance of the Hartshorn type. A main grain size was estimated from the line broadening of the peak by the Sherrers method. The grain size was estimated to be approximately 80 nm.

3. Results and discussion

Figure 1 shows the X-ray powder spectra for alignment and pressed sample. The curves c and d in Fig. 1 show the effect of heat treatment on the diffraction patterns of materials milled for the time 120 h. The patterns before milling (curves

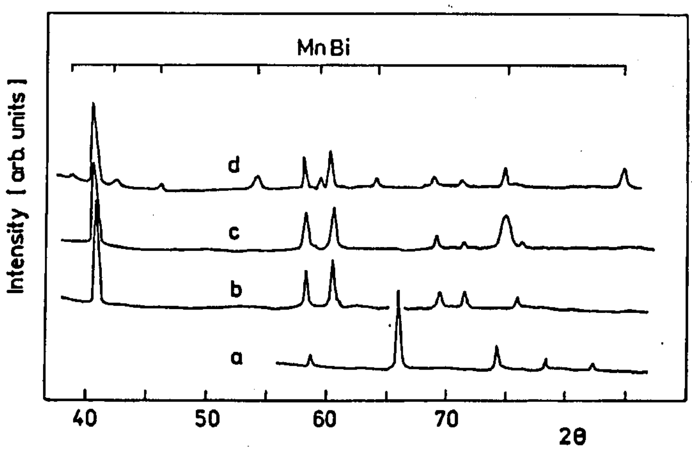

Fig. 1. X-ray diffraction patterns of as-milled, mechanically alloyed MnBi powders.

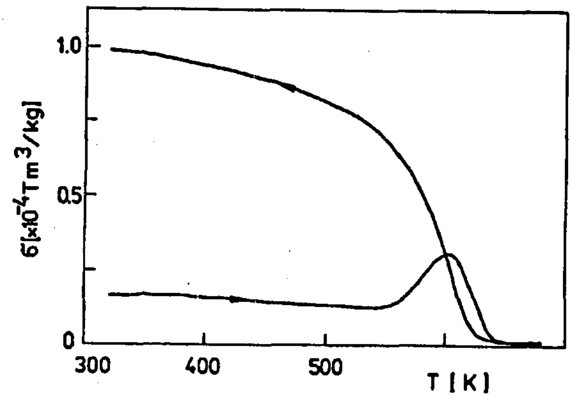

Fig. 2. The thermomagnetic curves for MnBi mechanically alloyed after 120 h milling.

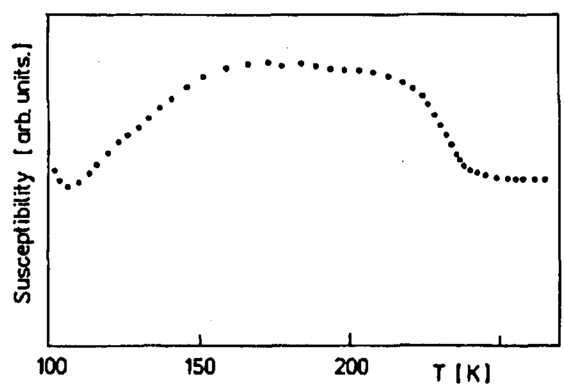

Fig. 3. Temperature dependence of the measured initial susceptibility of MnBi powders after mechanical alloying.

a and *b*) are shown for comparison. It can be seen from the curve *c* that the line ($2\Theta = 75$ degs) due to a fine microstructure of MnBi has decreased and has been converted (curve *d*) into a hexagonal phase. Shultz et al. [4] observed a similar change in the X-ray diffraction (XRD) patterns from NdFeB samples. Another line in the curve *c* represents a diamagnetic Bi matrix.

Figure 2 shows the magnetization vs. temperature curves for a MnBi powder sample. The magnetic phase MnBi is formed by a heat treatment. Because of the extremely fine microstructure of the milled powders the reaction can take place at relatively low temperature and with short reaction times. The maximum magnetization is obtained after annealing at 573 K for 20 minutes.

A temperature hysteresis occurs, so that ferromagnetism disappears at 633 K on heating and reappears at 613 K on cooling. In these compounds the structures are all the same, only at the temperature the distance between the Mn atoms varying. The fact that the point for Mn lies on the steep part of Bethe's curve agrees nicely with the fact that disappearance of ferromagnetism is associated with a sudden contraction of the lattice. Magnetic measurements were made in a magnetic field parallel to the alignment axis. The intermetallic compound MnBi is ferromagnetic with the saturation moment of about 1.0×10^{-4} T m^3/kg. The equilibrium phase at room temperature is hexagonal and is generally known in the recent literature as the low-temperature phase (LTP) to distinguish it from a high-temperature phase (HTP) stable above 613 K [5]. The structure and composition of the HTP are slightly different from the LTP. In our samples the third phase exists at low temperature. This phase is referred to as the new phase (NP) or as the high coercive (HC) phase of the MnBi. NP phase has the Curie temperature of 513 K. Our initial susceptibility data in Fig. 3 indicate that both the phases coexist in at least some of the particles. In the samples frozen at moderate rates, only a part of the Mn is presented as LTP MnBi. At least a part of the remaining Mn is present in the NP form, which is ferromagnetic with the saturation moment comparable to LTP [6].

4. Conclusions

The present work has demonstrated that mechanical alloying is an effective technique of the synthesis of intermetallic compound MnBi.

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