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The ferromagnetic transition in MnAs synthesised by mechanical alloying and powder blending techniques

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A study of the structure and properties of MnAs synthesized by mechanical alloying and powder blending techniques has been carried out. Mechanical alloying resulted in the formation of MnAs during milling. Following heat treatment samples prepared using both techniques exhibited a magnetostructural transformation from the paramagnetic B31 to the ferromagnetic $B8_1$ phase with decreasing temperature or increasing magnetic field. The transformation temperatures and fields were found to depend on milling procedure and heat treatment conditions. Powder blended and heat treated samples exhibited excellent stability during transformation cycling.

1. Introduction

The ferromagnetic compound MnAs has recently received renewed attention since it was shown to exhibit potentially important properties for a variety of magnetic [1] and magnetoelectronic applications [2]. MnAs is well known to exhibit a Curie temperature at $T_c = 320$ K associated with a first order transformation from the ferromagnetic hexagonal NiAs-type ordered phase ($B8_1$, space group $P6_3/mmc$) to a paramagnetic orthorhombic MnP-type ordered phase (B31, space group Pnma) [3, 4] during heating. A large lattice volume contraction, the presence of thermal and/or magnetic field hysteresis and a high magnetic field sensitivity of the Curie temperature are characteristic features of this transition [1, 5, 6]. A giant magnetoelastic response near room temperature resulting from the magnetostructural transformation has been recently reported [6].

Bulk MnAs has been conventionally prepared by melting of the constituent elements [7]. The high vapor pressure and toxicity of As requires that stringent safety precautions be employed. The use of mechanical alloying for the low temperature synthesis of a wide range of materials has been the subject of considerable study in recent years [8]. During mechanical alloying the repeated deformation, welding and fracture of reactant particles during ball-powder collision events have been shown to result in the formation of homogeneous alloys from elemental starting powders. In this work we distinguish between mechanical alloying, which results in the *in-situ* synthesis of alloys by high-energy ball-milling, and the powder blending procedure which mixes and activates the reactants for subsequent heat treatment at elevated temperatures. Powder blending essentially includes thorough mixing and particle size reduction. Particle deformation may occur, however, *in-situ* synthesis reactions do not take place. In this paper we report the results of a study of the transformation behaviour of MnAs synthesized using both mechanical alloying and powder blending techniques.

2. Experimental procedure

The starting materials used in this study were 99.9% pure Mn (−50 mesh) powder and 99.9998% pure As pieces crushed into coarse powder with a particle size less than 0.5 mm. Mechanical alloying was performed using a SPEX 8000 mixer/mill for times ranging from 2 to 24 hours. A sealed argon filled hardened steel vial and stainless steel balls of 9.5 mm diameter were used. The ball-to-powder mass charge ratio was 10 : 1. Powder blending was carried out in a sealed argon filled 160 mm diameter cylindrical plastic vessel which was rotated by means of rollers at 40 RPM for 24 hours. Zirconia balls of 10 mm diameter were used and the charge ratio was 20 : 1. All powder handling was carried out in a glove-box filled with high purity Ar gas (O_2 and H_2O <3 ppm).

The as-prepared powders were compacted under 1.5 GPa into cylinders of 5 mm height in a 5 mm diameter die inside the glove-box and then hot pressed under vacuum at 523–573 K and 1.5 GPa for 1–2 hours. Post-consolidation annealing of 0.5–1.5 hours duration was performed in argon at constant temperatures in the range of 573–1073 K. The final density was greater than 95% of theoretical. The chemical compositions

measured by X-ray fluorescence analysis under vacuum were $Mn_{52.5}As_{47.5}$ and $Mn_{52}As_{48}$ for the ball-milled and powder blended specimens, respectively.

The structure of the as-prepared powders and specimens was examined by electron microscopy using a Philips EM430 transmission electron microscope, by X-ray diffraction using a Siemens D5000 diffractometer and by optical microscopy. Magnetic measurements were performed in a vibrating sample magnetometer (VSM 3001, Oxford Instruments) equipped with a 12T superconducting solenoid. The temperature and magnetic field ramps were conducted at 5 K/min and 200 Oe/s, respectively. The hysteresis loops were corrected for demagnetisation. The ferromagnetic transition was also characterised by calorimetric (Perkin-Elmer DSC-4) and thermal expansion (NETZSCH 402EP) measurements.

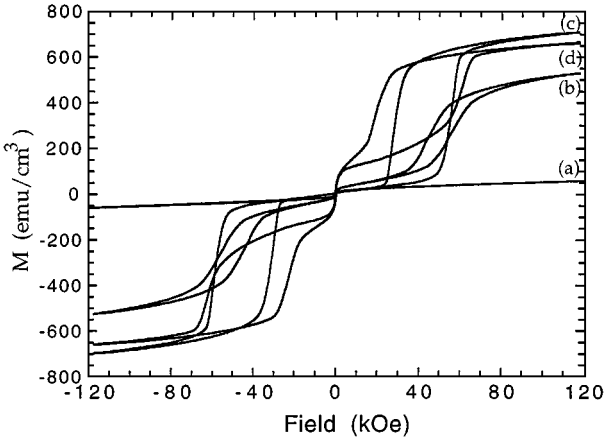

Figure 2 Magnetisation curves at $T = 292$ K for mechanically alloyed MnAs: (a) as-milled; (b) hot-pressed; (c) annealed 623 K/1.5 h; (d) annealed at 773 K/0.5 h.

3. Results and discussion

3.1. Mechanically alloyed samples

X-ray diffraction patterns of samples mechanically alloyed for 12 hours are shown in Fig. 1. Mechanical alloying for 12 hours resulted in the formation of MnAs having the orthorhombic MnP-type phase. Additional minor peaks corresponding to an unidentified intermediate phase were also present. After hot pressing only peaks associated with MnAs were present. Apart from peak sharpening, further heat treatment had little effect on the diffraction patterns. A minor Mn peak was present in all of the heat treated samples.

The effect of heat treatment on the magnetization curves of the mechanically alloyed samples is shown in Fig. 2. The magnetisation curves of the as-milled samples showed a very small ferromagnetic component near $H = 0$, which was due to contamination from Fe picked up during milling. In samples which were hot pressed, or hot pressed and heat treated at 623 K an abrupt increase in magnetisation was observed on reaching a critical field. This increase in magnetisation is associated with the field induced transformation from the paramagnetic B31 phase to the ferromagnetic $B8_1$ phase. On decreasing the field, the reverse $B8_1 \rightarrow B31$ transformation occurred at a lower field than the forward transformation. Both the change in magnetisation and the field hysteresis between the forward and reverse transformations increased with increasing heat treatment temperature.

In Fig. 3 measurements of the temperature dependence of the low field ($H = 1$ kOe) magnetisation are shown for the hot pressed sample. The abrupt increase in magnetisation at ~270 K during cooling is associated with the forward ferromagnetic transformation. This value of the Curie temperature is almost 40 K lower than values previously reported in the literature for MnAs [1, 2, 4, 5, 9]. A similar depression of T_c in mechanically alloyed MnAs has been recently reported by Wee *et al.* [10]. The decrease in T_c in mechanically alloyed samples appears to be due to the partial substitution of Fe in MnAs during heat treatment. In the present study the Fe content of mechanically alloyed samples is estimated to be 0.43wt% Fe. The effect of small composition changes on martensitic transformation temperatures is well documented in MnAs and other alloys [11]. With MnAs, partial substitution of Fe appears to be useful tool for shifting T_c towards lower temperatures.

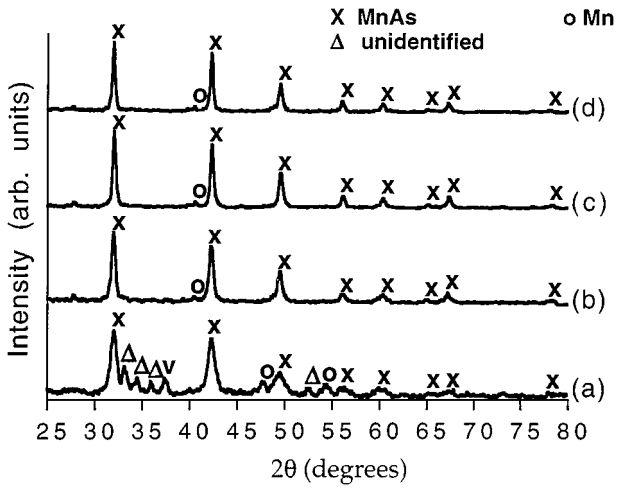

Figure 1 X-ray diffraction patterns of mechanically alloyed MnAs: (a) as-milled for 12 h; (b) after hot-pressing at 573 K; (c) hot pressed and annealed at 623 K for 1.5 h; (d) hot pressed and annealed at 773 K for 0.5 h.

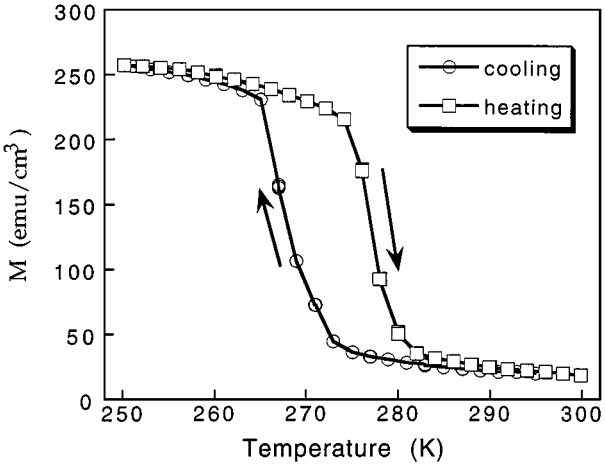

Figure 3 Magnetisation vs temperature for mechanically alloyed and hot-pressed MnAs ($H = 1$ kOe).

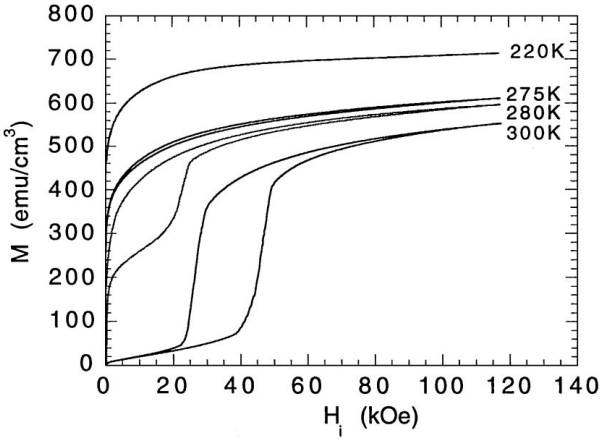

Figure 4 Effect of temperature on magnetisation curves for hot pressed mechanically alloyed sample heat treated at 623 K.

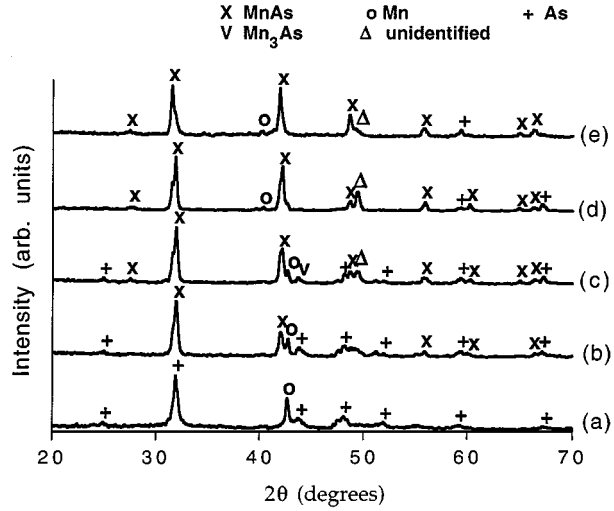

Figure 5 X-ray diffraction patterns of powder blended MnAs: (a) as-blended; (b) hot-pressed at 573 K; (c) annealed at 623 K for 1.5 h; (d) annealed 773 K for 0.5 h; (e) annealed at 1073 K for 0.5 h.

Measurements of the effect of temperature on the magnetisation curves for a sample heat treated at 623 K are shown in Fig. 4. In the ferromagnetic phase (below 270 K) values of M_s equal to 700 emu/cm^3 and coercivities equal to ~350 Oe were obtained. As these samples were nearly single phase (Fig. 1), the change in magnetisation may be taken as approximately equal to the saturation magnetisation, M_s, of the ferromagnetic phase, in good agreement with values previously reported in conventionally prepared MnAs [5, 9].

The critical fields for the forward and reverse magnetic transitions were found to increase linearly with increasing temperature in agreement with the Clausius-Clapeyron relation for magnetic field induced first order phase transitions. The magnetic field dependence of equilibrium Curie temperature T_c^{eq} was determined to equal 0.59 K/kOe [10]. As shown in Fig. 4, both M_s and the field hysteresis, ΔH, decrease with increasing temperature. This behaviour has been shown [6] to be due to the tricritical behaviour of MnAs associated with the second order transformation to the paramagnetic NiAs-type phase at ~410 K.

3.2. Powder blended samples

X-ray diffraction curves corresponding to various stages in the preparation of the powder blended samples are shown in Fig. 5. As would be expected, only diffraction peaks corresponding to elemental Mn and As were present after powder blending. Hot pressing and heat treatment at 773 K were required to remove the major compositional non-uniformities in the powder blended samples. While MnAs was present after hot pressing, the samples heat treated below 773 K were still inhomogeneous, containing As, Mn, Mn_3As and the unidentified intermediate phase which was present in the mechanically alloyed samples. Minor peaks corresponding to Mn, As and the intermediate phase were still present in samples heat treated at 773 K and 1073 K.

Magnetisation measurements carried out on powder blended samples after hot pressing and heat treatment are shown in Fig. 6. All samples exhibited ferromagnetic behaviour at room temperature. At temperatures above the Curie temperature, the samples exhibited a

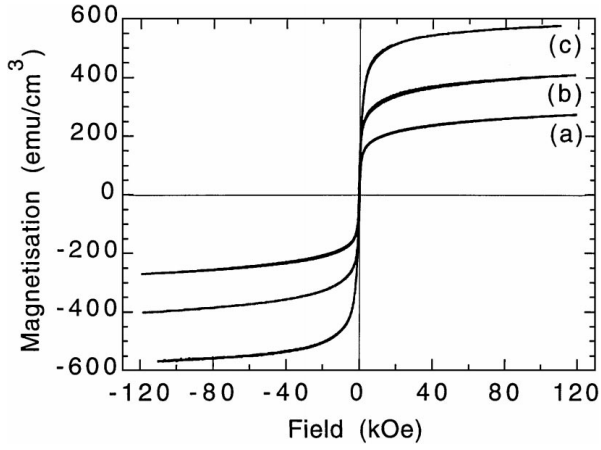

Figure 6 Magnetisation as a function of magnetic field at 292 K for powder blended MnAs: (a) hot-pressed; (b) hot pressed and annealed at 623 K; (c) hot pressed and annealed at 773 K.

paramagnetic to ferromagnetic transition on reaching a critical field, similar to that observed in the mechanically alloyed samples. However, the lack of compositional uniformity of the powder blended samples resulted in reduced values of saturation magnetisation relative to the mechanically alloyed samples. For samples heat treated at 773 K, measurements of the effect of temperature on the critical transformation field gave $dT/dH = 0.62$ K/kOe [6], in good agreement with the mechanically alloyed samples. The powder blended samples exhibited a T_c of 313 K, in good agreement with previous studies of MnAs [1, 2, 4, 5, 9]. Since ceramic grinding balls were used in preparing the powder blended samples, the higher value of T_c relative to the mechanically alloyed samples may be taken as further evidence that T_c for the mechanically alloyed samples was reduced by the presence of Fe originating from the ball mill.

3.3. Effect of transformation cycling

For both the mechanically alloyed and powder blended samples, cycling resulted in no change to the magnetic

properties or transformation temperatures. This behaviour differs from that observed in alloys which exhibit thermoelastic martensitic transformations, where transformation cycling has been shown to significantly influence transformation temperatures or stresses [12]. Changes in transformation behaviour accompanying cycling generally result from changes in internal elastic stress fields. The elastic stress fields developed during a diffusionless structural transformation are associated with volume changes and transformation shear. The transformation stresses are well known to result in localised plastic deformation which in turn modifies the elastic stress fields. It may be argued that with MnAs the brittle nature of the compound precludes any plastic deformation which would change the elastic stress fields induced by the transformation.

The ferromagnetic transformation in MnAs is accompanied by a volume contraction of approximately 2%. The dilatation components dominate the transformation strain tensor relative to the deviatoric components. As strains of this magnitude can clearly generate stresses exceeding the elastic limit, the occurrence of cracking and fracture accompanying the transformation was investigated by metallographic examination. The mechanically alloyed samples were observed to crack into numerous small pieces after only a few transformation cycles. On the other hand, a sample prepared by powder blending did not exhibit any evidence of cracking after 50 transformation cycles. It is possible that the additional phases present in the powder blended sample may have modified local stress fields such that crack initiation did not occur, however, further studies are required before any conclusions can be reached.

4. Conclusions

Mechanical alloying of Mn and As powders followed by hot pressing at 523 K resulted in the formation of MnAs. The mechanically alloyed samples exhibited a transformation from the paramagnetic B31 phase to ferromagnetic $B8_1$ with decreasing temperature or increasing magnetic field. The critical field required to induce the transformation increased with increasing temperature, in agreement with the Clausius-Clapeyron relation. Samples prepared by powder blending required heat treatment to form MnAs. Comparison of Curie temperatures for the mechanically alloyed and powder blended samples indicated that incorporation of Fe from the ball mill in the mechanically alloyed samples caused a significant reduction in T_c. Transformation cycling had negligible effect on the measurements of T_c. Powder blended samples exhibited an excellent resistance to transformation induced cracking, as compared to mechanically alloyed samples.

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