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Preparation of nanocrystalline Mn–Al–C magnets by melt spinning and subsequent heat treatments

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Abstract

$Mn_{54}Al_{44}C_2$ ribbon samples have been prepared by melt spinning in a single-phase ε hexagonal disordered state and its exothermal transformation at around 500 °C into a tetragonal $L1_0$ type magnetic structure (τ-phase) was followed by DTA, DSC, X-ray diffraction and thermomagnetic measurements. The metastable τ-phase stabilized by carbon addition could be transformed reversibly into the ε-phase at around 800 °C, without decomposition into the stable Al_8Mn_5 and β manganese phases. The almost constant Curie temperature obtained for partially transformed two-phase samples indicated a compositionally invariant transformation. By grinding the thin (25 μm) ribbon into sub-millimeter flakes, a bulk anisotropic magnet could be compacted by magnetic field oriented powder technology.

Keywords: Permanent magnets; Liquid quenching; X-ray diffraction; Thermal analysis; Magnetic measurements

1. Introduction

Manganese–aluminum alloys slightly above the equiatomic composition are an attractive permanent magnet material, exhibiting both high performance (superior mechanical strength and excellent machinability) and cost saving (free of precious elements). The good magnetic properties derive from the formation of a metastable $L1_0$ intermetallic phase (tetragonal τ-MnAl) characterized by strong, uniaxial magnetocrystalline anisotropy (10^6 J/m^3) with an "easy" *c*-axis [1]. The manganese ions are ferromagnetically aligned on (0 0 0) sites whilst on the body centered (1/2, 1/2, 1/2) sites they are anitiferromagnetically coupled with respect to the former. The aluminium ions occupy the remaining (1/2, 1/2, 1/2) sites [2]. Unfortunately, the $L1_0$(or τ)-phase is a metastable one forming from a quenched-in high-temperature hexagonal (ε) parent phase by annealing at 550 °C. The addition of a small amount of carbon stabilizes the tetragonal $L1_0$ phase and prevents the decomposition of the alloy into the stable but nonmagnetic γ (Al_8Mn_5) and β (Mn) phases. The stabilized τ-phase can also be obtained by slow cooling (<8 °C/min) from the temperature interval where the ε-phase is stable (from above 800 °C). The parent hexagonal disordered ε-phase is antiferromagnetic (T_N = 97 K) [3] with a distance between nearest neighbor Mn atoms equal to 2.698 Å. This distance is only slightly smaller than the atomic spacing in the magnetic τ-phase 2.769 Å [4].

The magnetic properties of τ-Mn–Al–C alloys depend on the microstructure and are strongly influenced by the τ-phase formation mechanism. Two modes of τ-Mn–Al–C formation have been proposed so far. A "flower-like" modification results from a massive transformation: hcp (ε)/fcc/fct (τ) [5], whereas a plate-like modification forms by a shear reaction: hcp (ε)/ε′/fct (τ) [6], where ε′ is an intermediate ordered orthorhombic phase. These transformation mechanisms have been studied so far on massive samples and probably both are valid but in different composition regions. The best magnetic properties [$(BH)_{max}$ = 64.4 kJ/m^3] have been obtained by high-temperature extrusion of a Mn–Al–C alloy [7].

The aim of this work was to study the phase transformations on a $Mn_{54}Al_{44}C_2$ ribbon sample obtained by melt spinning. It is expected that the magnetic properties are enhanced for the thin (25 μm) ribbon samples due to the homogeneity, fine grain size, increased solubility and fine dispersion of precipitates, which are attributes of liquid quenching technology.

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2. Experimental procedure

The $Mn_{54}Al_{44}C_2$ alloy ingot was prepared by vacuum induction melting under argon atmosphere. High-purity elements were placed in a water-cooled copper boat and held above the melting point to homogenize the ingot. The as-prepared ingot was used to prepare ribbon samples by a single-roller melt-spinning technique under protective atmosphere at a wheel speed of 25 m/s. Brittle and non-magnetic ribbons of about 24 μm in thickness and about 3 mm wide were produced. The evolution of the microstructure of the as-spun samples was examined by X-ray diffraction (Philips, Cu Kα radiation). Differential thermal analyzer (Setaram) and differential scanning calorimeter (Perkin-Elmer TGA7) were used to study the structural transformations up to the melting point. A Faraday balance equipped with a furnace up to 800 °C was used for thermomagnetic measurements.

3. Results and discussions

DTA and DSC measurements were carried out to find a proper annealing regime for the as-quenched non-magnetic ribbons. Fig. 1 presents the DTA diagram of an as-quenched ribbon. The DTA curve exhibits only one sharp exothermal peak around 500 °C corresponding to the structural transformation of the quenched-in ε-phase to the magnetic τ-phase. The endothermic peak around 800 °C corresponds to the transformation of the τ-phase back into the non-magnetic ε-phase. Two atomic percentage of carbon stabilizes the τ-phase and prevents the decomposition into non-magnetic β-manganese and γ-Al_8Mn_5. The melting around 1230 °C is manifested also in an endothermic peak.

Using DSC measurements with different heating rates (Fig. 2), we calculated the activation energy (E_a) for the formation of the τ-phase from a Kissinger plot (Fig. 3), where the logarithm of heating rate multiplied by the inverse of the square of the peak temperature is represented as a function of the inverse of the peak temperature. An activation energy of $E_a = 2.06$ eV was found which is rather low since the usual values for non-equilibrium alloys range between 1 and 5 eV.

X-ray diffraction measurements (Fig. 4) of the as-cast ribbons revealed that the $Mn_{54}Al_{44}C_2$ composition was quenched completely into the high-temperature stable hcp ε-phase. No

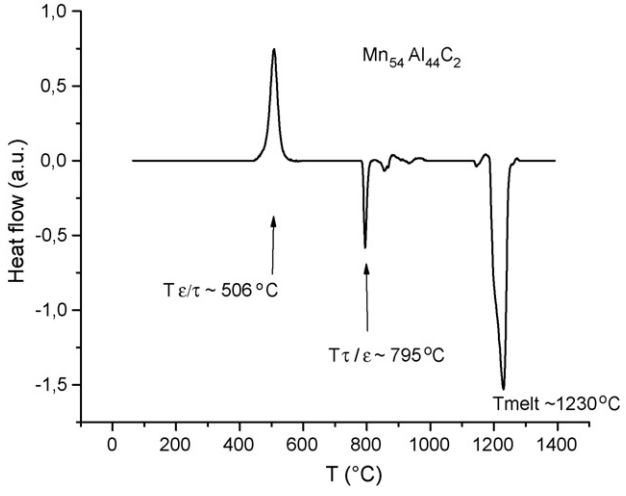

Fig. 1. DTA curve of the as-quenched $Mn_{54}Al_{44}C_2$ ribbon applying a heating rate of 20 K/min.

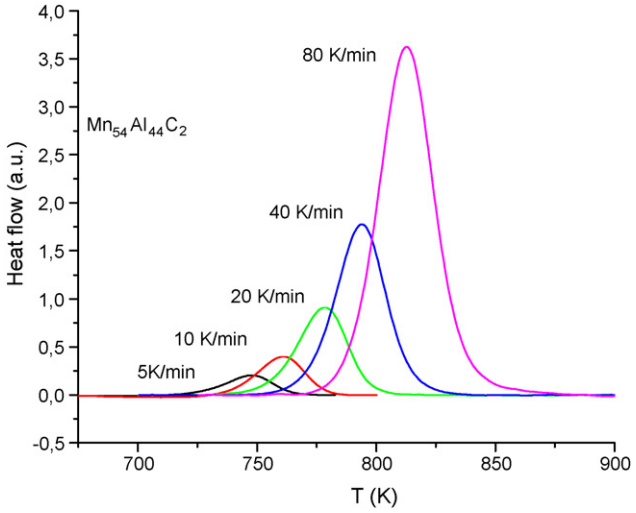

Fig. 2. DSC curves at various heating rates.

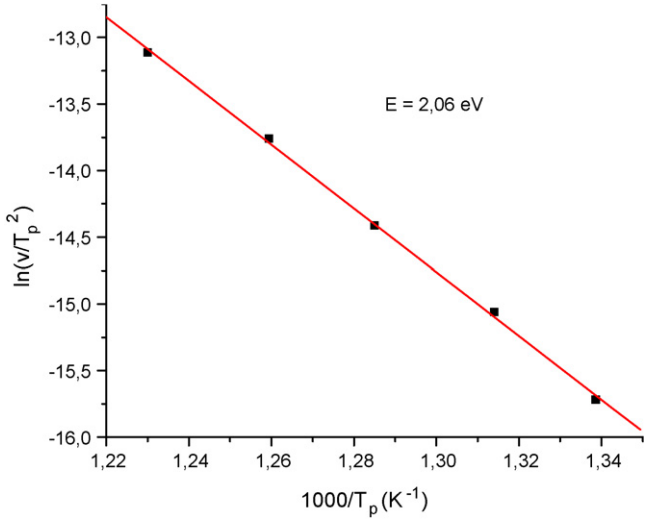

Fig. 3. Kissinger plot for determination of the activation energy for ε–τ transformation.

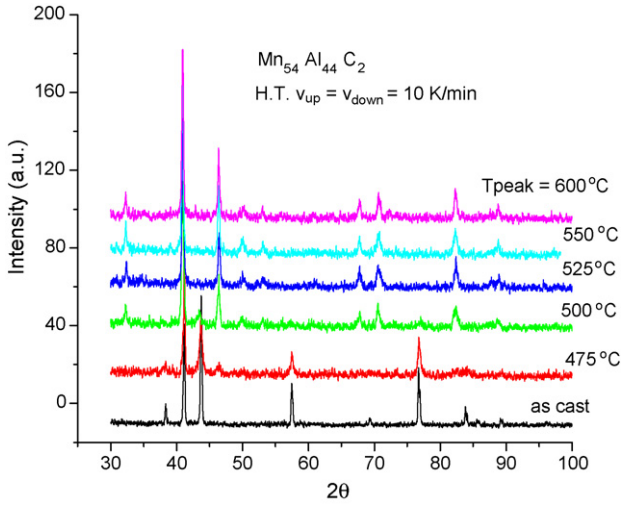

Fig. 4. X-ray diffractograms for the as-cast and heat-treated samples.

Table 1
The evolution of magnetic properties for partially transformed samples as a function of the peak temperature applied during the heating and cooling cycles

	B_s (T)	B_r (T)	H_c (kA/m)	$(BH)_{max}$ (kJ/m^3)
500 °C	0.563	0.30	129	9.6
525 °C	0.587	0.32	142	11.2
550 °C	0.60	0.34	133	12
600 °C	0.60	0.34	134	12

diffraction lines attributable to any other phase were present in the pattern. By cycling the sample between room temperature and the selected T_{max} indicated in Fig. 4, one can observe the emerging τ-phase lines, for example, the (1 1 0) at 32.3° and the (2 2 0) at 67.7°. Both the X-ray diffraction line intensity and the magnetization (Table 1) saturate with annealing temperature.

Because the τ-phase is the only ferromagnetic phase in the Mn–Al system, the saturation magnetization, M_s, of the alloy can be used to estimate the amount of τ-phase in the partially transformed sample. In our case, the highest value of M_s was 95 emu/g, which corresponds to 0.6 T (by taking the density as 5.1 g/cm^3). Moreover, its T_c can be also studied because it is below the annealing temperature so no further transformation can be expected during the T_c measurement. The thermomagnetic curves shown in Fig. 5 have been determined in a relative low magnetic field of only 25 kA/m. This field is far below that needed to saturate the sample, so it was suitable for the "kink point measurement" of the Curie temperature. The Curie temperatures being around 247 °C were determined as the inflection point of the ferro-paramagnetic transition curves. It is remarkable that for all the annealing temperatures, similar T_cs have been found indicating the same chemical composition of the ferromagnetic phase, regardless of its partial volume fraction. This is an argument in favor of a massive transformation mechanism [5], which occurs via a compositionally invariant diffusional nucleation and growth process.

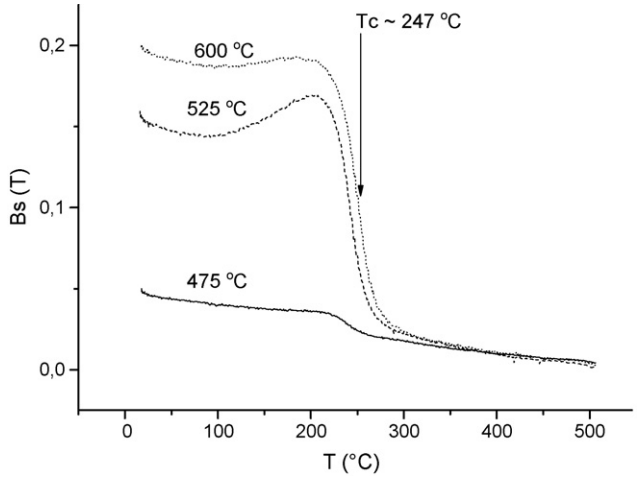

Fig. 5. Thermomagnetic curves to determine the Curie temperatures for partially transformed samples.

We have found that the highest coercivity is obtained by a rapid "up-quench" just at the ε to τ transformation temperature (around 500 °C), where the smallest grain size is obtained which is around 100 nm as can be estimated from the X-ray diffraction line width. Repeated heating up to the same temperature does not severely alter the magnetic parameters: the saturation magnetization remains constant around 0.6 T, the remanence around 0.31 T, and the coercivity around 130 kA/m. The coercive field achieved in this ribbon sample and in general for this material is low compared to the 2400–4000 kA/m anisotropic field of the pure τ-phase crystal [7]. Thus, it seems that the pinning of the domain walls at grain boundaries and other defects is the dominant mechanism for coercivity.

These magnetic property data are much below to those obtained for anisotropic bulk material prepared by hot extrusion at 750 °C [8] ($M_s \sim 0.7$ T; $B_r \sim 0.61$ T; $H_c \sim 240$ kA/m). Nevertheless, this brittle ribbon can serve as a precursor material for obtaining bulk magnets via powder technology. Applying mild grinding, flakes of several 100 μm can be prepared without introducing noticeable plastic deformations and hence no increased disorder, which diminishes the magnetic saturation and remanence.

The flakes were aligned in a natural rubber matrix applying an external magnetic field of 1 T. For the maximum loading, this rubber–$Mn_{54}Al_{44}C_2$ composite sample exhibits good flexibility and a saturation magnetization of 0.45 T, which corresponds to a filling volume of 75%.

In summary, isotropic ribbons of ferromagnetic τ-phase of a $Mn_{54}Al_{44}C_2$ alloy have been prepared by melt spinning and subsequent heating above the ε to τ transformation point (~500 °C). Flakes of such ribbon are suitable for preparation of bulk composite powder magnets of any shape.

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