Phase stability and magnetic properties of the Heusler alloy Mn$_2$CuAl ribbons

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Received 4 November 2009, revised 8 January 2010, accepted 19 January 2010
Published online 26 February 2010

Keywords magnetic susceptibility, ferromagnetic alloys, Heusler alloy, metastable phases, melt spinning

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A new Mn-based Heusler alloy Mn$_2$CuAl has been synthesized by the melt-spinning method. It has an ordered bcc structure and is a ferrimagnet with a saturation moment of 1.44 $\mu_B$/f.u. at 5 K. The magnetization mainly comes from the contributions of the antiparallel aligned Mn spin moments. A compensation point is observed at 630 K, indicating the antiferromagnetism between the two Mn sublattices. The Curie temperature of the ribbons is 690 K. When heated to 740 K, the Mn$_2$CuAl ribbons completely decompose to a mixture of a tetragonal phase and a Cu$_9$Al$_4$ phase.

1 Introduction In recent years, studies of the Mn$_2$-based Heusler alloys have attracted much attention for their potential applications as new functional materials. The research interest mainly focuses on the half-metallic materials and ferromagnetic shape-memory alloys (FSMAs) in the Mn$_2$YZ alloys, where Y is a transition-metal element and Z is a main group element.

Mn$_2$VAI was the first half-metallic material observed in Mn$_2$-based Heusler alloys [1–4]. In succession, Mn$_2$Ga and Mn$_2$FeZ (Z = Al, Sb) [5, 6] have also been predicted as half-metals by theoretical and experimental studies. Meanwhile, Mn$_2$NiGa [7] and MnNiIn [8] have been reported as newly discovered FSMAs. All these make Mn$_2$-based Heusler alloys a promising family for investigating new materials and phenomena.

However, the properties of Mn$_2$CuZ, which has Cu as the Y atom, are still not quite clear. The Cu atom has a filled d subshell and leaves the 4s with one electron. This is different from other 3d elements like Fe or Co, which have an unfilled d subshell. It may be expected that the different electronic configurations will have an influence on their electronic structure and magnetic properties. Recently, Li et al. [9] studied the electronic structure of Mn$_2$CuAl theoretically. It shows a half-metallic antiferromagnetic character with a small contraction of the equilibrium lattice. However, the experimental data of Mn$_2$CuAl is still unavailable. In order to measure its magnetic properties, we have synthesized Mn$_2$CuAl using the melt-spinning method and investigated its crystal structure, phase stability, and magnetic properties.

2 Experimental methods The Mn$_2$CuAl ingots were prepared by arc melting the constituent elements in a high-purity argon atmosphere. The purity of the starting materials was 99.9% or higher. The ingots were melted at least three times for homogenization. The ingots were then wrapped in molybdenum foil and sealed in a quartz tube and annealed at 1073 K for 3 days under protection of an argon atmosphere. The melt-spun ribbons were prepared by a single-wheel technique with the substrate velocity ($V_s$) of 20 m/s, under protection of an Ar atmosphere. Then X-ray powder diffraction (XRD) with Cu K$_\alpha$ radiation was used to verify the crystal structure and to determine the lattice constants. The temperature dependence of the magnetization was measured using a vibrating-sample magnetometer (VSM). The magnetization curves were measured by a SQUID magnetometer with applied fields up to 5 T.

3 Results and discussion Figure 1 shows the XRD patterns of the precursor ingot and the melt-spun Mn$_2$CuAl ribbons. The as-cast sample is mainly tetragonal phase together with some impurities. There are no diffraction peaks from Heusler alloys present. However, in the pattern of the
melt-spun samples, a pure bcc phase is identified. It is known that the ordering of the Heusler alloys is indicated by the presence of the (111) and (200) superlattice reflections. They present the ordering between the (B, D) and (A, C) sublattices, respectively. The Heusler structure can be looked upon as four interpenetrating face-centred-cubic (fcc) lattices, which have four unique crystal sites, namely, A(0,0,0), B(1/2,1/2,1/2), C(1/2,1/2,1/2), D(1/2,1/2,1/2) in Wyckoff coordinates as shown in Fig. 2. When atomic disorder occurs, the two peaks will be weakened or vanish [10].

In Fig. 1, the two diffraction peaks (111) and (200) are clear, suggesting that an ordered structure is obtained in Mn₂CuAl ribbons. A similar result has also been observed in Ni₃FeGa, which presents a fcc structure in the as-cast state but forms an ordered bcc structure in the melt-spun ribbons [11]. By indexing all characteristic diffraction peaks, the lattice constant of Mn₂CuAl has been determined as 0.591 nm. In Mn₂CuAl, the two Mn atoms tend to occupy the A and B sites and the distance between them is 0.256 nm, which is much smaller than the 4.12 μB/f.u. in Cu₂MnAl [12]. The small distance will lead to a different magnetic structure in Mn₂CuAl compared with that of Cu₂MnAl.

The magnetization curves of Mn₂CuAl ribbons measured from 5 to 300 K are shown in Fig. 3. An obvious ferromagnetic character is observed. It is clear that the saturation magnetization decreases gradually with increasing temperature. The saturation moment at 5 K is 1.44 μB/f.u., which is much smaller than the 4.12 μB in Cu₂MnAl [13]. So it may be inferred that the spin moments of the Mn atoms in Mn₂CuAl are in antiparallel alignment, as has been reported [9]. In Mn₂CuAl, the Mn atoms enter the A and B sites and are nearest neighbors. The small distance between the two Mn atoms favors antiferromagnetic coupling between their moments. When a Mn atom enters the A site, its spin moment partly compensates that of Mn (B) and leads to a decrease of the total moment. Similar result has also been observed in Mn₂NiGa [7].

The inset of Fig. 3 shows the temperature dependence of the magnetization of Mn₂CuAl ribbons from room temperature to above 700 K. There is a minimum at about 630 K, which corresponds to a compensation point. Above this point the magnetization increases again and reaches a Curie temperature of 690 K. The compensation point primarily arises from the antiparallel magnetic coupling between the Mn (A) and Mn (B) sublattices. In Mn₂CuAl, the spin moment of Mn (A) is antiparallel to that of Mn (B). The contribution of Cu to the magnetization is small. So, the net magnetic moment is determined by the competition of the two Mn sublattices. Due to the different chemical surroundings, Mn (A) and Mn (B) have different spin moments and the temperature dependences of the magnetization from the

Figure 1 XRD patterns of the precursor ingot and as-spun Mn₂CuAl ribbons.

Figure 2 Crystal structure of the Heusler alloys. The unit cell has four crystal sites as the basis: A(0,0,0), B(1/2,1/2,1/2), C(1/2,1/2,1/2), and D(1/2,1/2,1/2) in Wyckoff coordinates.

Figure 3 Magnetization curves of the as-spun Mn₂CuAl ribbons measured at different temperatures in a field up to 5 T. Inset shows the temperature dependence of the magnetization of Mn₂CuAl.
two sublattices are different. The moments of the two Mn sublattices decrease with increasing temperature, and when approaching the compensation point, the magnetization of the two sublattices is comparable to each other and leads to a decrease of net magnetization. The \( T_C \) of Mn\(_2\)CuAl is around 690 K, which is comparable to other Mn-based Heusler alloys like Mn\(_2\)NiGa [7] and indicates that there exists strong exchange interactions between the Mn atoms.

In order to test the thermal stability of the Mn\(_2\)CuAl ribbons, we carried out DTA measurements. The DTA curve of Mn\(_2\)CuAl is shown in Fig. 4a. The heating rate is 10 °C/min. There is an obvious exothermic peak at about 740 K, which may result from the decomposition of the Mn\(_2\)CuAl ribbons. In order to test this, we annealed the Mn\(_2\)CuAl ribbons below and above this temperature (630 and 750 K), respectively, then quenched in ice water. Their XRD patterns are shown in Fig. 4b. It is clear that, after annealing at 630 K, the sample still keeps the bcc structure. There is no diffraction peaks from the secondary phase observed, suggesting that Mn\(_2\)CuAl is still stable at that temperature. When annealing at 750 K, the bcc phase disappears and a mixture of the tetragonal phase and the Cu\(_9\)Al\(_4\) phase is observed [13]. This coincides well with the huge exothermic peak around 740 K.

The magnetization curves of the samples annealed at different temperatures are presented in Fig. 5. It can be seen that annealing at 630 K has little influence on the saturation moment of Mn\(_2\)CuAl, the \( M_s \) of which is only a little higher than that of the as-spun sample. While the sample annealed at 750 K shows a drastic decrease in \( M_s \), which is only 0.11 \( \mu_B \) at 5 K. This may be attributed to the precipitated tetragonal phase, which has an antiferromagnetic ground state [14]. It has been found that in off-stoichiometric Cu\(_2\)MnAl, the large magnetoresistance mainly comes from the interfacial scattering at the mixtures of magnetic Cu\(_2\)MnAl phase and nonmagnetic Cu\(_9\)Al\(_4\) phase, in which the noninteracting Cu\(_2\)MnAl particles are embedded in the Cu\(_9\)Al\(_4\) matrix structure [15]. Here, Mn\(_2\)CuAl has a similar phase separation, so it may be expected that large magnetoresistance can also be observed in Mn\(_2\)CuAl melt-spin ribbons.

4 Conclusions The structure, magnetic properties, and thermal stability of Mn\(_2\)CuAl melt-spin ribbons have been studied. The metastable Heusler alloy Mn\(_2\)CuAl can be obtained by the melt-spinning technique and is a ferrimagnet with a saturation moment of 1.44 \( \mu_B \)/f.u. at 5 K. The magnetic moment mainly comes from the contributions of antiparallel aligned Mn spin moments. A compensation point is observed at 630 K in the M–T curve. The Curie temperature of Mn\(_2\)CuAl ribbons is 690 K, indicating that the exchange interactions between the 3d atoms is strong. Above 740 K, Mn\(_2\)CuAl ribbons will completely decompose to a mixture of a tetragonal phase and Cu\(_9\)Al\(_4\) phase. The magnetic moment at 5 K clearly decreases after the decomposition.

Acknowledgements This work is supported by the National Natural Science Foundation of China in grant no. 50671034 and the Natural Science Foundation of Tianjin grant no. 08JCYBJC09700.
References