Physica B 405 (2010) 2840–2843

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Structure and magnetic properties of Fe_2CoGe synthesized by ball-milling

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ARTICLE INFO

Article history:
Received 6 January 2010
Received in revised form
3 April 2010
Accepted 6 April 2010

Keywords:
Heusler alloys
Band structure
Magnetic properties
Ball-milling

ABSTRACT

A Heusler alloy Fe_2CoGe has been synthesized by the ball-milling method. Its structure and magnetic properties have been studied. The results suggest that ball-milling can be a possible way to produce new Heusler alloys. Both X-ray diffraction and DTA measurement evidenced the formation of a partly amorphous phase after milling for 25 h. It is found that highly ordered Fe_2CoGe can be obtained by annealing the as-milled powder at 1073 K, while a disordered A2 phase is resulted by annealing at 773 K. The magnetic properties of Fe_2CoGe are not very sensitive to the atomic disorder. Electronic structure calculation suggests a ferromagnetic ground state in highly ordered Fe_2CoGe and the total spin moment is $5.03\mu_B$/f.u., which agrees well with the experimental value of $5.06\mu_B$ for the sample annealed at 1073 K. It is also found that the atomic disorder does not strongly change the ferromagnetic coupling between Fe and Co moments and also the general structure of the DOS. So the total spin moment only slightly increases when atomic disorder occurs.

1. Introduction

Study of the Heusler alloys has increased obviously in recent years due to new phenomenon, such as half-metallicity and shape memory effect, in this alloy family [1–4]. The Heusler alloy crystallizes in an ordered body-centered-cubic (bcc) structure and has a stoichiometric composition of X_2YZ, where X and Y are transition metal elements, and Z is a main group element. Generally the Heusler structure can be looked on as four interpenetrating face-centered-cubic (fcc) lattices, in which the X and Y atoms occupy the A (0, 0, 0), B $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and C $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ sites, and Z atom occupies the D $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ site in the Wyckoff coordinates.

In the study of the Heusler alloys, melt-spinning technique has been widely used, which is a non-equilibrium process and can retain the meta-stable phase to room temperature [5,6]. So it is a promising way to investigate new functional materials in the Heusler alloys. Here, ball-milling is another non-equilibrium way to synthesize new meta-stable materials; however, there are only few reports on its application in the Heusler alloys. Robinson et al. reported that Cu_2MnAl can be prepared via a combination of mechanical alloying and heat treatment [7]. Later, Zhang synthesized a DO_3 type Fe_2MnGe phase by annealing the as-milled amorphous powder at 673 K [8]. A typical shape memory alloy Ni–Mn–Ga was also synthesized and interesting magnetic properties change has been found in it [9]. Till now, the Heusler alloys synthesized by ball-milling are mainly Mn-based. When some antisite disorder was introduced to the lattice by ball-milling, the Mn moments in different sites may form an antiparallel coupling which will decrease the total moment and influence other magnetic properties. So it is interesting to study the effect of ball-milling in Mn-free Heusler alloy Fe_2CoGe.

In this paper, we report the structure and magnetic properties of a new Heusler alloy Fe_2CoGe prepared by ball-milling. Since Co_2FeSi was predicted as a half-metallic ferromagnet (HMF) by Wurmehl et al. [10], the work on Fe_2CoGe which has similar composition with Co_2FeSi can also be helpful in searching for new HMFs.

2. Experimental details and computational method

Fe_2CoGe sample was prepared by ball-milling in a planetary ball mill from high purity powder components (99.9% or higher). The mass of the loaded initial powder is 8 g. The mixture was sealed in steel vial with balls of different diameters made of hardened steel under argon atmosphere in a glove box. The ball to powder weight ratio is 10:1. The milling time is 25 h, which is sufficient for the formation of the compound. The samples were pressed into discs and sealed in a quartz tube filled with high purity argon and then annealed at 773 and 1073 K, respectively. X-ray powder diffraction (XRD) with Cu Kα radiation was used to check the crystal structure and to determine the lattice constants. The magnetization curves were measured by a Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometer with applied field up to 5 T. The Curie temperature

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doi:10.1016/j.physb.2010.04.008

was measured by an AC susceptometer with an AC magnetic field of amplitude 5 Oe.

We carried out the electronic structure calculation using the density functional theory (DFT) plane-wave pseudopotential method [11,12]. The exchange-correlation function was based on the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA) potential [13]. The interactions between the valence electrons and ion cores were described as ultrasoft pseudopotentials, first introduced by Vanderbilt [14]. The cut off energy for plane waves is 500 eV for all the cases to ensure good convergence of the total energy. The self-consistent calculations employed a grid of 182k points from a $15\times15\times15$ mesh in the irreducible Brillouin zone. The convergence tolerance was set to 5×10^{-6} eV/atom.

3. Results and discussion

The XRD pattern of the samples milled for different times is shown in Fig. 1. It is clear that the XRD patterns change obviously with prolonged milling time. When milling for 1 h, the starting elemental powder is simply crushed together. The XRD pattern shows only the elemental peaks, which are somewhat broadened by the stress and reduction of the grain size. After 5 h, only the iron diffraction peaks are identified and other elemental peaks vanish. It is also found that the iron peaks have a broad shoulder and moves to the low angle end. This may indicate the formation of a bcc Fe–(Co, Ge) solid solution. When the milling time reaches 25 h, a broad high peak at about 44° and two small peaks at 65° and 82° are observed. These diffraction peaks indicate that a disorder bcc A2 phase is formed after 25 h ball-milling. The triangular shape of the main peak may be attributed to the formation of some amorphous phase in the A2 phase [8,15], as has been confirmed by subsequent DTA measurement. Another possibility for the broad peak is the stress introduced by ball-milling, which may lead to the distortion of the lattice.

The DTA curve of the Fe_2CoGe powder milled for 25 h is shown in Fig. 2. The heating rate is 20 °C/min. The huge exothermic peak around 450 °C corresponds to the crystallization of the amorphous phase in the as-milled Fe_2CoGe powder. This confirms the conclusion in preceding discussions.

In order to investigate the crystal structure after crystallization and the influence of different annealing temperatures, we tried annealing the as-milled powder at 773 and 1073 K, respectively. The former is close to the crystallization temperature and the latter is much higher above it. It may be expected that they will have different influence on the crystal structure as well as the magnetic properties.

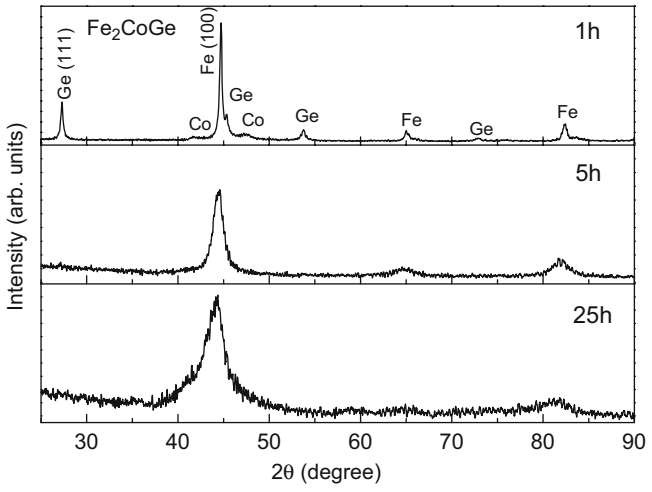

Fig. 1. XRD patterns of the Fe_2CoGe powder milled for different times.

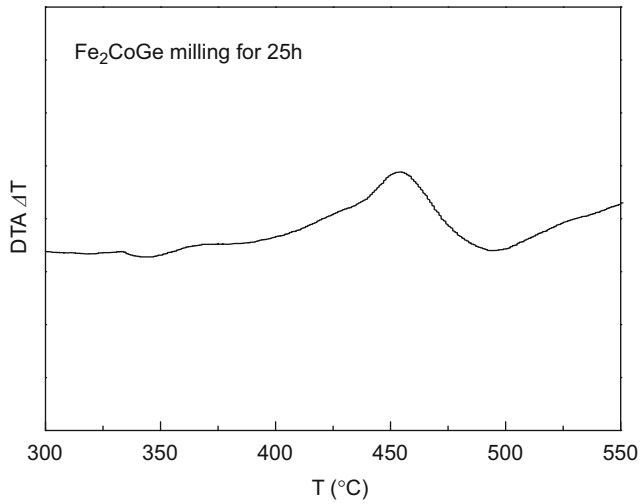

Fig. 2. Continuous-heating DTA curve at 20 °C/min of the as-milled powder of Fe_2CoGe.

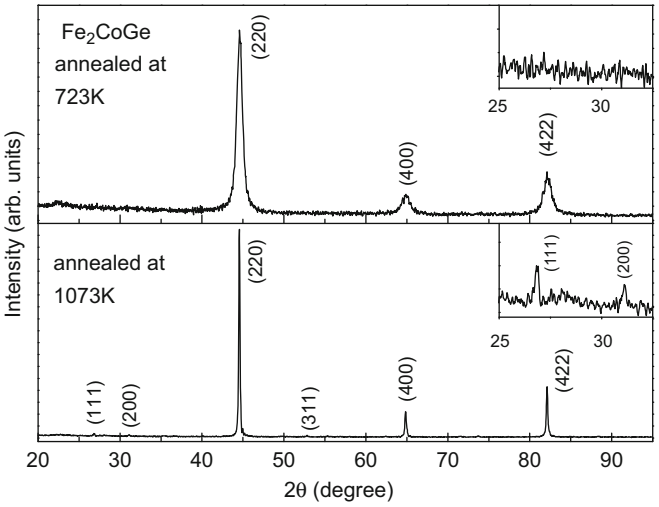

Fig. 3. XRD patterns of the Fe_2CoGe powder annealed at 773 and 1073 K, respectively.

Fig. 3 gives the XRD patterns of Fe_2CoGe powder annealed at 773 and 1073 K, respectively. It is clear that different annealing temperatures have no obvious influence on the basic structure. After annealing, the full width at half maximum (FWHM) decreases and the diffraction peaks become sharper compared with which of the as-milled powder. This is due to the increase of grain size and the elimination of the stress. In both cases, a bcc structure is retained. However, the annealing temperatures influence the atomic order in Fe_2CoGe strongly. For the sample annealed at 773 K, only three diffraction peaks: (2 2 0), (4 0 0), (4 2 2) are observed, indicating that a disordered A2 phase are formed. But for the sample annealed at 1073 K, superlattice diffraction peaks (1 1 1) and (2 0 0) are identified together with the main peaks. Since the (2 2 0) peak is too strong in the pattern, we show the detail in the insets of Fig. 3.

It is known that the ordered Heusler structure is represented by the existence of the superlattice reflections (1 1 1) and (2 0 0). Usually the (1 1 1) diffraction represents the order between the B and D sites, and (2 0 0) diffraction is corresponding to the order between the (A, C) atoms and B sites. So our results prove that an