Journal of Magnetics 16(1), 10-14 (2011) DOI: 10.4283/JMAG.2011.16.1.010

Two-Phase Magnet in the Co/Co_2MnSn System

Taewan Kim[1], Hye-in Yim[2], Hyun-Yong Lee[3], and Kyoung-il Lee[4]*

[1]*Department of Advanced Materials Engineering, Sejong University, Seoul 143-747, Korea*
[2]*Department of Physics, Sookmyung Women's University, Seoul 140-742, Korea*
[3]*Faculty of Applied Chemical Engineering, Chonnam National University, Kwangju 500-757, Korea*
[4]*Nano Convergence Device Center, Korea Institute of Science and Technology, Seoul 136-791, Korea*

(Received 20 August 2010, Received in final form 19 November 2010, Accepted 30 November 2010)

.This study reports on Co/Co_2MnSn two-phase magnets. The Co/Co_2MnSn two-phase magnet has Co precipitates in a Co_2MnSn Heusler alloy matrix, in which the two phases are exchange-coupled at the phase boundary. The as-casted Co/Co_2MnSn system, which has Co-Mn solid solution precipitates in a Co_2MnSn Heusler alloy matrix, showed that the Co solid solution precipitates are crystallographically coherent and there is exchange coupling at the phase boundary. To form pure Co precipitates by removal of Mn solute atoms in Co-Mn solid solution, annealing was carried out 48 hours at 870°C. After annealing, the low T_c and low magnetization phase of the Co-Mn solid solution became a high T_c and high magnetization phase of hexagonal Co.

Keywords : two-phase magnet, exchange coupling, Heusler alloy, metallic phase

1. Introduction

Two-phase magnets are a new class of phase-separated magnetic materials. In two-phase magnets, when the two phases are in intimate contact, exchange coupling becomes possible at the phase boundary. The two metallic-phase magnets consist of two metallic magnetic phases with a negative or positive exchange at the phase boundary. As an example, macroscopic ferrimagnet Co-TbN with a paramagnetic phase TbN in a ferromagnetic Co matrix was proposed for making magnetoresistive materials consisting of two suitably dispersed and mutual exchange-coupled phases [1]. A Co/Co_2TiSn system, with ferromagnetic Co_2TiSn Heusler alloy precipitates in a ferromagnetic Co matrix exhibited giant magnetoresistance (GMR), which is evidence of antiparallel exchange coupling at the phase boundary. A model of the wall formation at the phase boundary explains the GMR effect of the Co/Co_2TiSn two-phase magnet system [2]. In nano-structured dual magnets, the less the particle size decreases, the more the phase interface area to volume increases. Therefore, the interface effects at the phase boundary come become the main factors in determining the physical properties of two-phase materials. Nano-structured two-phase magnets are made through the combination of several magnetic materials, such as hard and soft ferromagnets, ferromagnets and paramagnets, and ferromagnets and antiferromagnets. Using the magnetic exchange coupling between two phases, well-designed two-phase magnets can provide opportunities to create new magnetic materials with highly efficient hard or soft magnetic properties, and novel properties that arise at the nanoscale.

Co/Co_2MnSn systems were studied in an effort to form two-phase magnets that exchange couple two metallic ferromagnetic phases at the phase boundary. We found that the two metallic phases consist of a low T_c, low magnetization phase (hexagonal Co solid solution) and a high T_c, high magnetization phase (Co_2MnSn). The Co solid solution precipitates in the Co_2MnSn Heusler alloy matrix. In this system, the Co solid solution precipitates are crystallographically coherent with the matrix. Annealing experiments showed that there was ferromagnetic exchange coupling at the phase boundary.

2. Experiments

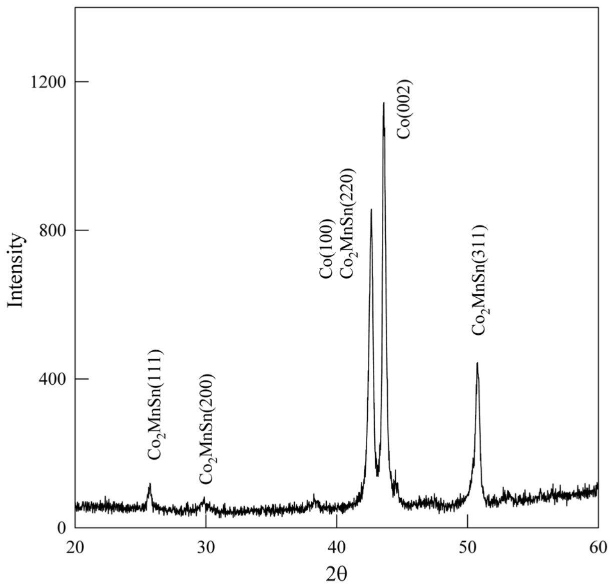
Ingots were prepared by arc melting in a commercial arc furnace with a water-cooled hearth and tungsten electrode. The chamber was evacuated by a mechanical pump and backfilled with argon several times. High-purity argon gas (99.999%) flowed through the chamber

*Corresponding author: Tel: +82-2-958-6851
Fax: +82-2-958-6627, e-mail: 201mail@gmail.com

continuously during arc melting. An analysis of the microstructures was made with backscattered electron and secondary electron images on a SEM and compositional analysis of the phases was carried out using energy dispersive x-ray (EDX) analysis. To analyze the sample compositions, a single-phase sample with the composition of Co_2MnSn served as a standard sample. The compositions of the samples were determined by comparing the EDX spectra of the samples with that of the Co_2MnSn standard sample. X-ray diffraction analysis characterized the samples with two phases. In the annealing experiments of as-cast bulk samples, the samples were annealed for 48 hours at 870°C in a N_2 atmosphere to prevent decomposition of the intermetallic compound by oxidation.

3. Results and Discussion

The phase equilibria in the Co/Co_2MnSn system were studied with composition along the pseudobinary join Co-Co_2MnSn in the ferromagnetic region. The Co_2MnSn Heusler alloy, with 50 at.% of Co, formed as a single phase. The Co particles started to precipitate in the Co_2MnSn matrix at the composition of Co_4MnSn. The magnetization of Co_2MnSn was large and increased with the Co concentration. Cobalt became the primary phase at more than 71 at.% of Co [Co_5MnSn] and crystallized out of a Co_2MnSn rich matrix. The volume fraction of Co phase increased with the Co composition in the composition range of Co_4MnSn to Co_7MnSn. The x-ray diffraction pattern and SEM image from Co_5MnSn sample in Fig. 1 show the formation of a stable two-phase magnet. Compared with the peaks from arc-melted pure Co and single-phase Co_2MnSn Heusler alloy, the diffraction peaks of Co_5MnSn matched those of hexagonal Co and $L2_1$ Co_2MnSn Heusler alloy [3]. All peaks from hexagonal Co shifted in this sample, which indicated the possibility that the Co precipitate was a solid solution of Co-Mn. The Co-Mn phase diagram shows 6% solid solubility of Mn in Co. The peaks from Co_2MnSn with typical Heusler alloy structure were not shifted. New lattice parameters were calculated using the shifted diffraction angles of the (100) and (002) peaks of hexagonal Co in the two phases. The c axis increased 2.2% to 4.17 Å and the a axis decreased 2.3% to 2.45 Å. Based on these two lattice parameters, the diffraction angles of other hexagonal Co peaks were calculated. These calculated angles were compatible with the observed hexagonal Co peaks in the two-phase magnet (Table 1). The (100) peak of hexagonal Co shifted to a higher diffraction angle and overlapped with the (200) peak of the Co_2MnSn Heusler alloy. The (002) peak of Co shifted to a smaller diffraction angle. The overlap of hexagonal Co and Co_2MnSn peaks and the shift of the hexagonal Co peak suggest that the Co phase and Co_2MnSn Heusler alloy phase are crystallographically coherent. The SEM image shows that the Co solid solution (dark image)



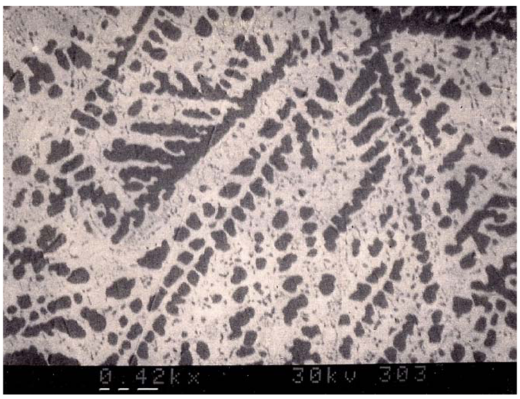


Fig. 1. The X-ray diffraction pattern and SEM image of Co_5MnSn with two phases (hexagonal Co and Co_2MnSn Heusler alloy).

Table 1. The observed and calculated diffraction angles of hexagonal Co precipitates in as-casted Co_5MnSn samples.

h k l	$2\theta_{pure}$	$2\theta_{obs}$	$2\theta_{cal}$
1 0 0	41.6	42.5	42.5
0 0 2	44.6	43.4	43.4
1 0 1	47.3	48	48.1
1 0 2	62.6	62.1	62.3
1 1 0	75.9	77.7	77.8
1 1 1	78.3	81.3	81.76

– θ_{pure}: Diffraction angles from pure hexagonal Co
– θ_{obs}: Diffraction angles from Co precipitates in Co/Co_2MnSn
– θ_{cal}: Diffraction angles obtained from new lattice parameters

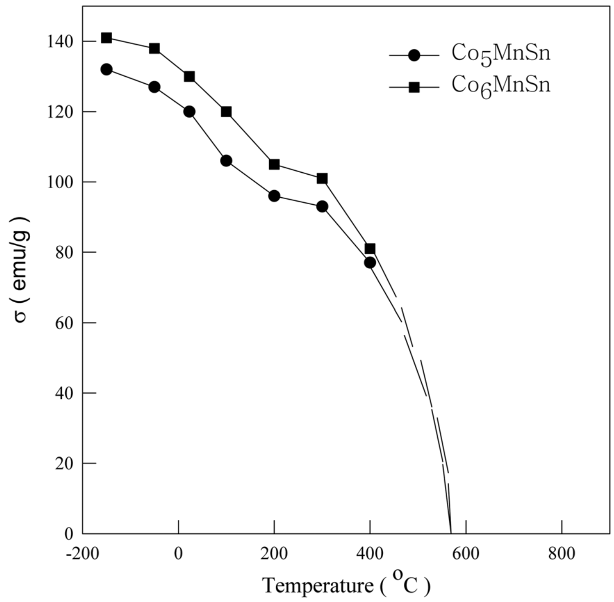


Fig. 2. Magnetization vs. temperature curves of the Co_5MnSn and Co_6MnSn samples with two Co/Co_2MnSn phases.

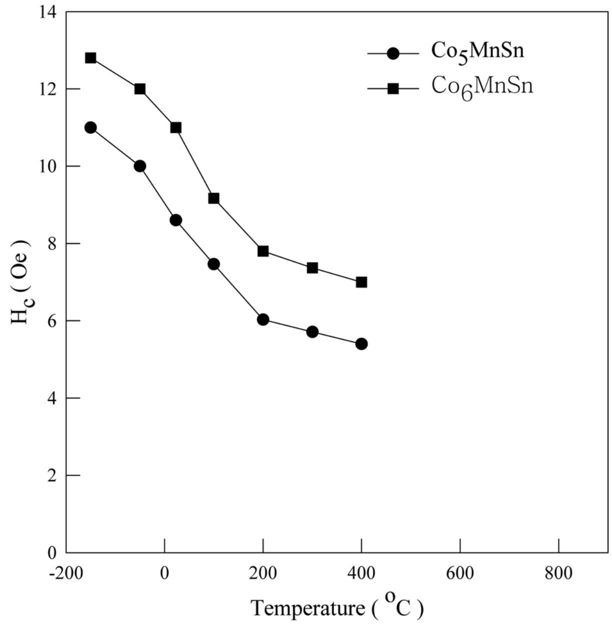


Fig. 3. Coercivity vs. temperature curves of the Co_5MnSn and Co_6MnSn samples with two-phase stable Co/Co_2MnSn.

precipitates in the Co_2MnSn Heusler alloy matrix (bright image).

Figs. 2 and 3 show the magnetization and coercivity vs. temperature in Co_5MnSn and Co_6MnSn compositions, respectively. The phase transformation from hexagonal Co to fcc Co takes place at around 430°C; therefore, this experiment was carried out in the range of −150 to 400°C. The T_c of the lower T_c phase can be estimated by extrapolating the high-temperature data to low temperatures. Fig. 2 shows that these samples contain two magnetic phases--one with low T_c and low magnetization and the other with high T_c and higher magnetization. Extrapolating the two curves of Co_5MnSn and Co_6MnSn to high temperature shows that the curves merge on the temperature axis. The temperature at this point was approximately 570°C, which is consistent with a T_c of 556°C of the Co_2MnSn Heusler alloy. The T_c of the hexagonal Co solid solution could be roughly estimated by extrapolating the two breakpoints separating the high and low Tc phases in the magnetization curve of Fig. 2. The Curie temperatures of the Co-Mn solid solution in the Co_5MnSn and Co_6MnSn samples were approximately 160 and 175°C, respectively. The increase in Mn concentration in the Co phase reduced the T_c, which is evidence of a Co-Mn solid solution.

Fig. 3 shows the coercivity in Co_5MnSn and Co_6MnSn samples as a function of temperature. The coercivity change with temperature was divided into two regions, with about 150°C in the center, as the case of magnetization vs. temperature. The coercivity at $T < 150$°C was that of the Co phase. The Curie temperatures, determined from the temperature at which H_c(T) changes slope, was about 180°C, which is in approximate agreement with the T_c from magnetization vs. temperature (Fig. 2). The as-casted single-phase Co_2MnSn Heusler alloy sample demonstrated a closed hysteresis loop without coercivity or remanence. In Fig. 3, there is extra coercivity at $T > 150$°C, where the Co_2MnSn phase is the only magnetic phase. This suggests that the extra coercivity at $T > 150$°C is associated with the exchange coupling of Co and the Co_2MnSn Heusler phase at the phase boundary.

Heusler alloys are defined as ternary intermetallic compounds, at the stoichiometric composition X_2YZ, which have the $L2_1$ structure [3]. In the Heusler $L2_1$ structure, the constituent atoms, which may carry a magnetic moment, can occupy simple cubic and body-centered and face-centered cubic sublattices. The majority of Heusler alloys order ferromagnetically. If the Y site is occupied by Mn, it is in the alloy X_2MnZ. Typical Z site elements are In, Sn, Sb, Al, Ge, or Ga. Common X site elements are Cu, Co, Ni, Pd, Pt, or Rh [4]. The magnetic properties of these alloys arise from the magnetic moments on transition-metal atoms, located on either the X or Y sites. Most commonly, the moments on the X sites are associated with Co atoms while the moments on the Y sites are associated with Mn atoms. In the series Co_2MnZ, the magnetic moment from the Mn sites is $4\mu_B$ and a substantial moment is associated with the Co sites. This results in an increase in the exchange interactions and

Table 2. The calculated and observed relative intensities of Co_2MnSn Heusler alloy matrix in as-casted Co_5MnSn samples.

h k l (2θ)	I_{hkl}/I_{220} (cal.)	I_{hkl}/I_{220} (obs.)
111* (25.2)	12.16	14.77
200** (29.7)	3.79	12.63
220 (42.6)	100	100
311* (50.5)	5.02	9.2
222** (52.8)	1.1	8.35
400 (61.8)	15.12	19.6
420** (70.2)	1.24	8.56
422 (78.1)	27.3	27.08

– Column 2: Calculated relative intensities of Co_2MnSn Heusler alloy
– Column 3: observed relative intensities of Co_2MnSn Heusler alloy matrix

correspondingly higher Curie temperature [5, 6]. When the Heusler alloy has a highly ordered structure, superlattice peaks have some high intensities. If Mn and Sn atoms are disordered in the Heusler alloy structure, the x-ray diffraction peaks from (111) and (311) planes disappear. On the other hand, if Co, Mn and Sn atoms are disordered, the peaks from (200), (222) and (420) peaks disappear. The structural factors can be changed by the formation of vacancies at the Co and Mn sites in the Co_2MnSn Heusler alloy structure, which causes the decreases the intensity of the primary peaks and increases the superlattice peaks. Table 2 shows the calculated and observed relative intensities of the Co_2MnSn Heusler alloy matrix obtained from the Co_5MnSn sample. The observed

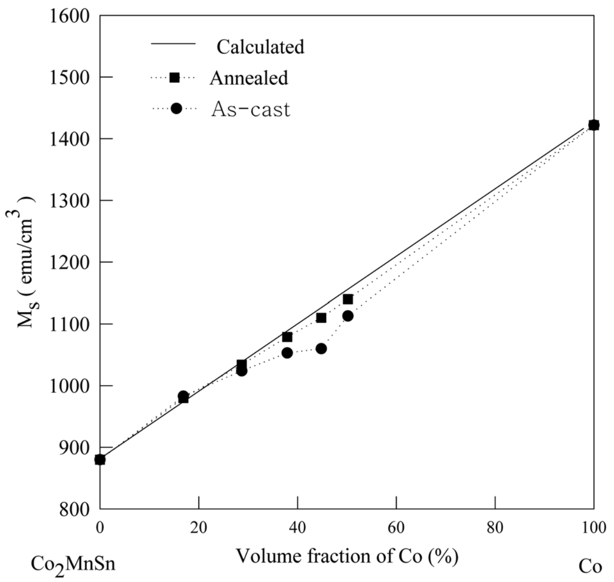


Fig. 4. Saturation magnetization, M_s (emu/cm^3), as a function of the volume fraction of Co to Co_2MnSn for experimental magnetizations (before and after annealing) to the calculated magnetization.

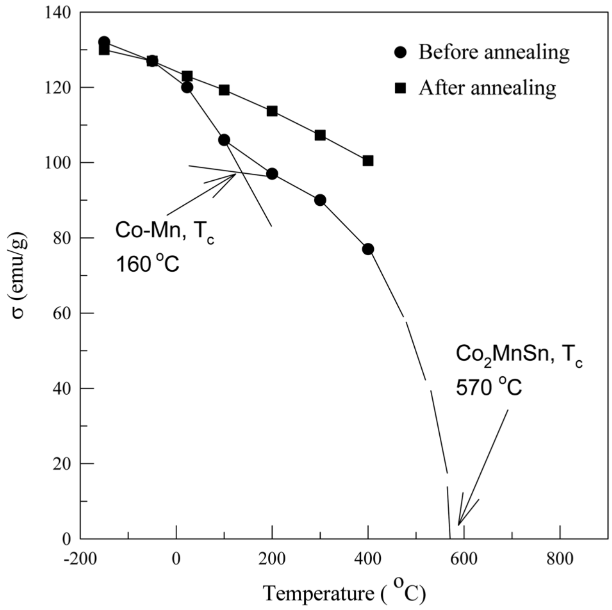


Fig. 5. Magnetization vs. temperature of Co_5MnSn with two phases before and after annealing.

relative intensities of superlattice peaks were much higher than the calculated relative intensities. The Co_2MnSn Heusler alloy matrix has a highly ordered structure and there are many vacancies in the Co and Mn sites.

Fig. 4 shows the saturation magnetization vs. volume fraction of Co to Co_2MnSn before and after annealing. Before annealing, the magnetization of the samples with two phases was smaller than the calculated magnetization, based on the volume fraction of Co to Co_2MnSn. If the Mn atoms, which are antiferromagnetically exchange coupled to Co atoms, were dissolved in the Co precipitates, this could explain the deviation of the experimental magnetization from the calculated magnetization before annealing. After annealing, as the Mn atoms were removed from Co precipitates, the experimental magnetizations became close to the calculated magnetizations. Fig. 5 shows the magnetization vs. temperature curves of Co_5MnSn with two phases before and after annealing. As-casted samples showed two magnetic phases; from the breakpoint, one has low T_c and low magnetization and the other high T_c and high magnetization. The high T_c magnetic phase was the Co_2MnSn Heusler alloy phase and the low Tc magnetic phase was Co-Mn solid solution precipitates. The breakpoint separating the high and low T_c phases vanished by annealing. This means that the Co precipitate phase changes from the low T_c and low magnetization Co-Mn solid solution phase to the high T_c and high magnetization phase pure Co phase, with Mn atoms removed from precipitates by annealing.

4. Conclusion

A stable Co/Co_2MnSn two-phase magnet, consisting of metastable Co-Mn solid solution precipitates in a Co_2MnSn Heusler alloy matrix, was formed at the composition > 71 atomic % of Co. Both phases were crystallograpically coherent and exchange coupled at the phase boundary. Extra coercivity at $T > 150^{o}C$ and the Co composition dependency of the Curie temperature indicated that exchange coupling occurred at the phase boundary. The precipitates in Co_2MnSn Heusler matrix were a metastable Co-Mn solid solution. The Co_2MnSn Heusler matrix had a highly ordered structure and many vacancies in the Co and Mn sites. Annealing decreased the vacancy concentration of the Heusler alloy matrix and the metastable Co-Mn solid solution became nearly pure Co.

Acknowledgements

This work was supported by the fund of the Korea Institute of Technology (2E21492-09-306) and the Korea Research Foundation Grant, funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2008-313-D00428).

References

[1] Taewan Kim and Jung Keun Oh, J. Magnetics **13**, 11 (2008).
[2] Taewan Kim and Jung Keun Oh, J. Magnetics **13**, 43 (2008).
[3] H. P. J. Wijn, Magnetic Properties of Metals, Springer-Verlang, New York (1991) p. 168.
[4] C. C. M. Campbell, J. Phys. F: Metal Phys. **5**, 1931 (1975).
[5] P. J. Webster and K. R. A. Ziebeck, J. Phys. Chem. Solids **34**, 1647 (1973).
[6] P. J. Webster, J. Phys. Chem. Solids **32**, 1221 (1971).