Magnetic properties and phase stability of Co$_2$(Ti$_{1-x}$Mn$_x$)Ga Heusler alloys

A Okubo$^1$, R Y Umetsu$^1$, R Kainuma$^1$ and K Ishida$^2$

1 Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan.
2 Department of Materials Science, Graduate School of Engineering, Tohoku University, 02 Aoba-yama, Sendai 980-8579, Japan.

E-mail: rie@tagen.tohoku.ac.jp (RY Umetsu)

Abstract. Magnetic properties and phase stability of the $L_2^1$ phase in Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys were investigated by magnetic and DSC measurements. The order-disorder phase transition temperature from the $L_2^1$ to the $B_2$ phase $T_{t L_2^1/B_2}$ was found to increase linearly with increasing Ti composition and its linear extrapolation to $x = 0.0$ accords with the reported value of $T_{t L_2^1/B_2}$ for the Co$_2$TiGa alloy. The Curie temperature $T_C$ increases with increasing Mn composition, exhibiting an upward convexity, but is rather independent of composition in the high Mn region. It is concluded that the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys located in the middle composition range possess both a high $T_C$ and a high $T_{t L_2^1/B_2}$.

Introduction

Half-metallic ferromagnets (HMFs) have been intensively investigated in the field of spintronics because they are promising candidates for spin-dependent devices such as magnetic random access memory and magnetoresistive read-head devices. Theoretical investigations have reported that many Co-based Heusler alloys with a full-Heusler ($L_2^1$)-type structure exhibit a perfect or a high spin polarization at the Fermi energy ($E_F$) [1-3]. From the viewpoint of applicability, in addition to the spin polarization and Curie temperature $T_C$, the phase stability of the $L_2^1$ phase is also important. In fact, it has been reported in magnetic tunnel junctions (MTJs) using Co-based Heusler alloys, such as Co$_2$Mn(Al$_{1-x}$Si$_x$) [4], Co$_2$(Cr$_{1-x}$Fe$_x$)Al [5,6] and Co$_2$Fe(Al$_{1-x}$Si$_x$) [7,8], showing a large tunnel magnetoresistance (TMR) ratio, that the as-sputtered phase shows an amorphous or disordered structure, such as $A2$ and $B2$, and that the heating process to increase the degree of $L_2^1$ order sometimes brings about a decrease of the TMR ratio due to phase separation and/or roughening of the layer surfaces through chemical diffusion [4,8]. If the $L_2^1$ phase is very stable, there is a possibility that an $L_2^1$ single-phase layer is obtained even in as-sputtered condition and that formation of an $L_2^1$ layer with a smooth surface, which may be suitable for the ferromagnets in the MTJ, is expected without additional annealing after spattering. Therefore, it is important to seek a new HMF with a high stability of the $L_2^1$ structure.

The stability of the $L_2^1$ phase can be thermodynamically evaluated with order-disorder phase transition temperature from the $L_2^1$ to the $B2$ phase $T_{t L_2^1/B_2}$. We have previously investigated the magnetic properties and the phase stability of the $L_2^1$ phase in pseudo-binary Co$_2$(Ti$_{1-x}$Fe$_x$)Ga alloys in order to develop new applicable materials with both high $T_{t L_2^1/B_2}$ and high $T_C$, since among the Co$_2$YGa ($Y = Ti, V, Cr, Mn$ and Fe) ternary alloys, the Co$_2$TiGa and the Co$_2$FeGa show the highest $T_{t L_2^1/B_2}$ and...
$T_c$, respectively [9]. In that study, it was concluded that coexistence of a relatively high $T_{t/L_2/B_2}^{12/82}$ and a high $T_c$ is achieved in the Co$_2$(Ti$_{0.5}$Fe$_{0.5}$)Ga alloy [10].

In the present study, in order to seek another new applicable material the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys were selected, because as well as Co$_2$FeGa, the Co$_2$MnGa alloy also has a high $T_c$ [11], and the magnetic properties and phase stability of their alloys were examined.

**Experimental procedure**

Alloys were obtained by induction melting under an argon gas atmosphere. The specimens were annealed at 1373 K for 3 days and quenched in water. The microstructure of the obtained specimens was observed with a optical microscope, and the crystal structure of the obtained specimens was identified by x-ray powder diffraction (XRD) measurement using Cu-$K\alpha$ radiation. Lattice constants were refined with the Rietveld method. The order-disorder phase transition temperature was determined by differential scanning calorimetry (DSC) of a heating and cooling rate of 10 K/min. Magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM) of a heating rate of 2 K/min.

**Results and discussions**

Figure 1 (a) shows XRD patterns at the room temperature for Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys quenched from 1373 K, together with the calculated patterns for the $L_2_1$-type structure with a perfect degree of order in $x = 0.25$ and 0.90 by using the RIETAN-2000 program [12]. The intensities of the superlattice reflections 111 and 220 are in good agreement with the calculated values, indicating that all the specimens have a fully ordered $L_2_1$-type structure. Concentration dependence of the obtained lattice constants are indicated in Fig. 1 (b). Lattice constants exhibit a linear dependence on the concentration, in accordance with the data in the literature for $x = 0.0$ (Co$_2$TiGa) [13-15] and $x = 1.0$ (Co$_2$MnGa) [11,15,16] alloys.

DSC heating and cooling curves for $x = 0.85$, 0.90 and 0.95 alloys are shown in Fig. 2. As seen in the DSC curves, some endothermic peaks corresponding to transformations are observed, as indicated by closed circles and triangles. By comparison with the experimental thermomagnetization curves obtained from the same specimens, it can be confirmed that the endothermic peak detected at the lower temperature (▲) is associated with the $T_c$. On the other hand, base on DSC measurements and transmission electron microstructural (TEM) observations, it has been reported that the $T_{t/L_2/B_2}^{12/82}$ for $x = 1.00$ (Co$_2$MnGa) is located at 1195 K [9,16]. Based on this, the endothermic peak at the higher temperature (●) is identified as the disordering reaction at the $T_{t/L_2/B_2}^{12/82}$. The $T_{t/L_2/B_2}^{12/82}$ for the alloys below $x = 0.8$ cannot be experimentally determined because the $T_{t/L_2/B_2}^{12/82}$ becomes higher than the melting point of the alloy.

![Figure 1](image_url)

**Figure 1.** (a) X-ray diffraction patterns measured at room temperature for Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys, together with calculated patterns of $L_2_1$ phase for $x = 0.25$ and 0.90. (b) Concentration dependence of the lattice constants for Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys, together with the reported values for $x = 0.0$ [13-15] and 1.0 [11,15,16].
Figure 3 shows the concentration dependences of $T_{L^2/B^2}$ and $T_C$ for the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys determined from the DSC and the thermomagnetization curves, together with the values reported for the stoichiometric Co$_2$TiGa and Co$_2$MnGa alloys [9,10,16]. It is seen that the $T_{L^2/B^2}$ exhibits a linear concentration dependence reaching the value reported for $x = 0.0$ (Co$_2$TiGa). Such a linear behaviour of $T_{L^2/B^2}$ has been reported in other quaternary Co-based Heusler alloys of Co$_2$(Cr,Fe)Ga [17], Co$_2$(V,Mn)Ga [16], and Co$_2$Mn(Al,Si) [18]. On the other hand, as indicated by the closed triangles in Fig. 3, the $T_C$ increases with increasing $x$ with an upward convexity, being rather independent of $x$ in the concentration range above $x = 0.70$. This result is curious because the saturation magnetization at 4.2 K measured for the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys in the present investigation almost linearly increases with increasing $x$, as following the Slater-Pauling behaviour [2]. According to recent theoretical calculations on the effective exchange constant of Co$_2$MnZ ($Z =$ Si, Sn and Ge) alloys [19], the atomic distances between the magnetic atoms also affect the value of $T_C$. Therefore, the concentration dependence of the $T_C$ may be explained as being due to the combined effects of the concentration dependences in the magnetic moment and the lattice constant. Such a convex behaviour of the concentration dependence of $T_C$ has been also observed in the Co$_2$(Cr,Fe)Ga [17], Co$_2$(V,Mn)Ga [16], and Co$_2$(Ti,Fe)Ga [10] alloys.

Figure 2. DSC heating and cooling curves for Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys. Closed circles and squares indicate the order-disorder phase transition temperature from the $L^2_1$ to the $B^2$ phase $T_{L^2/B^2}$ and the Curie temperature $T_C$, respectively.

Figure 3. Concentration dependence of the order-disorder phase transition temperature from the $L^2_1$ to the $B^2$ phase $T_{L^2/B^2}$ and the Curie temperature $T_C$ for the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys, together with those for the stoichiometric Co$_2$TiGa and Co$_2$MnGa alloys [9,10,16].
In summary, the order-disorder phase transition temperature from the $L_2_1$ to the $B_2$ phase $T_{t_{L_2_1/B_2}}$ and the magnetic properties of Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys were investigated by means of DSC and magnetic measurements. The $T_{t_{L_2_1/B_2}}$ increases with increasing Ti composition (i.e., 1-$x$) and the linear extrapolation to $x = 0.0$ accords with the $T_{t_{L_2_1/B_2}}$ reported for the Co$_2$TiGa alloy. The $T_C$ increases with increasing $x$ with an upward convexity, and is independent of the composition above $x = 0.70$. It is concluded that having both a high $T_c$ and a high $T_{t_{L_2_1/B_2}}$, namely, a high phase stability in the $L_2_1$, the Co$_2$(Ti$_{1-x}$Mn$_x$)Ga alloys located in the middle composition range are a good candidates for applicable materials.

Acknowledgments

This study was supported by Grants-in-Aid from Core Research for Evoloutional Science and Technology (CREST), the Japan Science and Technology Agency (JST), and from the Japanese Society for the Promotion of Science (JSPS), by a Grant-in-Aid for Scientific Research (S), No. 18106012, and by the Global Center of Excellence (GCOE) Project. A part of this work was carried out at the Center for Low Temperature Science, Institute for Materials Research, Tohoku University.

References

[1] Kübler J, Williams AR and Sommers CB 1983 Phys. Rev. B 28 1745.
[2] Galanakis I and Dederichs PH 2002 Phys. Rev. B 66 174429.
[3] Ishida S, Sugimura S, Fujii S and Asano S 1991 J. Phys. Condens. Mat. 3 5793.
[4] Oogane M, Sakuraba Y, Nakata J, Kubota H, Ando Y, Sakuma A and Miyazaki T 2006 J. Phys. D Appl. Phys. 39 834.
[5] Inomata K, Okamura S and Tezuka N 2004 J Magn. Magn. Mater. 282 269.
[6] Marukame T, Ishikawa T, Hakamata S, Matsuda K, Uemura T and Yamamoto M 2007 Appl. Phys. Lett. 90 012508.
[7] Tezuka N, Ikeda N, Miyazaki A, Sugimoto S, Kikuchi M and Inomata K 2006 Appl. Phys. Lett. 89 112514.
[8] Tezuka N, Ikeda N, Miyazaki A, Okamura S, Kikuchi M, Sugimoto S and Inomata K 2007 J. Magn. Magn. Mater. 310 1940.
[9] Kobayashi K, Ishihika K, Umetzu RY, Kainuma R, Aoki K and Ishida K 2007 J. Magn. Magn. Mater. 310 1794.
[10] Okubo A, Umetzu RY, Nagasako M, Fujita A, Kainuma R and Ishida K 2008 Scripta Mater. 59 830.
[11] Webster PJ 1971 J. Phys. Chem. Solids 32 1221.
[12] Izumi F and Ikeda T 2000 Mater. Sci. Forum 321 198.
[13] Sasaki T, Kanomata T, Narita T, Nishihara H, Note R, Yoshida H and Kaneko T 2001 J. Alloys Comp. 406 317.
[14] Ziebeck KRA and Webster PJ, 1974 Phys. Chem. Solids. 35 1.
[15] Buschow KHI, van Engen PG and Jongebreur R 1983 J. Magn. Magn. Mater. 38 1.
[16] Umetzu RY, Kobayashi K, Fujita A, Kainuma R, Ishida K, Fukamichi K and Sakuma A 2008 Phys. Rev. B 77 104422.
[17] Umetzu RY, Oikawa K, Kobayashi K, Kainuma R, Ishida K, Endo N, Fujita A, Fukamichi K and Sakuma A 2005 Phys. Rev. B 72 214412.
[18] Umetzu RY, Kobayashi K, Fujita A, Kainuma R and Ishida K 2008 Scripta Mater. 58 723.
[19] Kurtulus Y, Dronskowski R, Samolyuk GD and Antropov VP 2005 Phys. Rev. B 71 014425.