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Study of the structural and magnetic properties and gallium exchange phenomenon in a Mn-Ga alloy doped by Cr during the milling and annealing process

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ABSTRACT

The effect of milling and annealing process on Cr doped Mn_3Ga nanocrystallite has been investigated. Phase determination analysis shows that Ga turning to get out of Mn-Ga structure and tend to make bonding to Cr and form Cr_3Ga_4 product during milling process. Annealing of the new phases lead to decomposition of Cr_3Ga_4 and formation of a new Mn-Ga phase in reverse direction, in the other words diffusion of Ga atoms occurs from Cr_3Ga_4 to Mn phase and α-Mn and Cr_3Ga_4 change to Mn_3Ga_2 and Cr phases. The variation of coersivity, magnetization and magnetic state of different samples was explained according to the crystallite size of the present phases and grain boundary effects. It was also confirmed that formation of Mn-Cr clusters plays an important role in increase of saturation magnetization.

1. Introduction

Some of Mn_xGa compounds with high Curie temperature, high spin polarization and high anisotropy have great potential for industrial applications [1–7]. Mn_3Ga is one of the most interesting compounds. Theoretically Mn_3Ga is a full Heusler compound which is crystallized in $L2_1$ crystal structure [8]. Experimentally it has been synthesized in cubic (disordered Cu_3Au-type structure) [9], hexagonal ($D0_{19}$) [10] and tetragonal ($D0_{22}$ & $L1_0$) structures [3,11,12]. An anomalous Hall Effect has been observed for the tetragonal distorted lattice in the crystallographic $D0_{22}$ phase by Glas et al. [13].

Some of ternary compounds of Mn-Ga-X show interesting properties such as Mn-Ga-Ni which shows ferromagnetic shape-memory effect [14–17]. Also some researchers are still trying to synthesize Mn-Ga compounds with a higher coercivity and saturation magnetization. The magnetic properties of Mn_xGa thin films have been studied on different substrate [18,19]. The uniaxial anisotropy can increase if Mn_3Ga films grow on Cr seed layers [1,20]. The results of these reports show a reduction of anisotropy in Mn_3Ga ultrathin films on Cr substrate depends on layer thickness. Low Co content in Mn-Ga-Co leads to additional strain that reduces the anisotropy [21]. In another work, $Mn_{3-x}GaCo_x$ Heusler alloys shows soft-magnetic hysteresis loops [22].

Previously, the influences of the diffusion of Mn and Cr atoms in cobalt ferrite nanoparticles is investigated and higher values of the coercive field of Mn and Cr substituted cobalt ferrite is attributed to lower average particle size [23]. First principle FLAPW calculations performed on Mn_2CrZ (Z=Al, Ga, Si, Ge and Sb) alloys showed a large and localized magnetic moment on Cr site, which is antiparallel to the moment of Mn and this is a key note to find new half-metallic antiferromagnets in Heusler alloys [24]. Also the itinerant magnetic properties for ζ_2-GaM (M=Cr,Mn) have been already studied [25]. Method of preparation affects the magnetic properties. In Mn_3Ga compound synthesized by arc-melting method, if it anneals at 400–450 °C, the obtained saturation magnetization and anisotropy will be the highest degree [12].

In this paper, we studied the effects of Cr doping on magnetic property of Mn_3Ga compound. Cr has antiferromagnetic property similar to Mn while the interatomic distance for Cr is smaller. According to Bethe–Slater curve, the exchange interaction between the moments of two similar 3d atoms changes by atomic distance. By addition of Cr to the milled Mn_3Ga compound, a new multiphase sample is obtained and its magnetic property is studied. Annealing of this sample changes the composition of the material and it affects the magnetic property.

2. Experimental

Mn_3Ga alloy was prepared by arc-melting of Mn pieces (0.99%,

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Aldridge) and Ga ingots (0.99%, Aldridge) in Argon atmosphere. Then a high energy shaker mill (Spex 8000) was used for 15 h ball milling of the crashed Mn_3Ga. Two series of samples was prepared by milling of mixtures of Mn_3Ga+Cr. Two different weight ratio (Mn_3Ga/Cr) of 2 and 10 and different milling time (0, 0.5, 2 and 5 h) was considered. To study the effects of thermal treatment, one sample was annealed for 60 h at 350 °C in a tubular vacuum furnace. The crystal structure of the samples was examined by X-ray diffraction (XRD) at room temperature using Cu $K\alpha_1$ and $K\alpha_2$ radiation. The crystal structures were refined by Rietveld analysis. The magnetic properties were measured by a vibrating sample magnetometer (VSM) at room temperature.

3. Results and discussion

The XRD pattern of 15 h milled Mn_3Ga is shown in Fig. 1. It verifies that the 15 h milled sample has been crystallized in tetragonal structures. The main phase of the compound is Mn_3Ga while a little amount (less than 5%) of Mn_4Ga and Mn_2Ga also exist in the sample. Mn_3Ga and Mn_4Ga have been crystallized in a $L1_0$ tetragonal structure whit P/4 mmm space group and the c/a ratio is 1.002 and 0.999 respectively. Another phase, Mn_2Ga has been crystallized in a $D0_{22}$ tetragonal structure with I/4 mmm space group and $c/a=1.868$. VSM analysis measurement for 15 h milled Mn_3Ga showed a saturation magnetization of 0.194 ± 0.007 Am^2/Kg and coercivity of 0.018 ± 0.002 T. Slater-Pauling rule predicts that the X_2YZ Heusler materials with 24 valance electrons per unit cell have zero magnetization. A saturation magnetization around zero has been reported for Mn_3Ga with $L1_0$ structure [12]. One may expect no magnetization for Mn_4Ga with a similar structure to Mn_3Ga while some of sites for nonmagnetic Ga atoms are vacant.

The XRD patterns and Rietveld refinement results of the Mn3Ga-50 wt% Cr after 30 min, 2 and 5 h milling are shown at Fig. 2. It can be concluded from Fig. 1 that before milling process there should be a mixture of Cr, Mn_3Ga, Mn_4Ga and Mn_2Ga phases in Mn3Ga-50 wt% Cr sample. In the 30 min milled sample, the Mn_2Ga phase disappeared, the Mn_3Ga phase content decreased while an increase of the Mn_4Ga phase was observed and a new phase of Cr_3Ga_4 was formed. It seems that Mn-Ga bounds have been broken by milling process and Cr-Ga bounds have been formed. This phenomenon is also observed for 2 and 5 h milled samples. After 5 h milling of the sample, all of Mn-Ga compounds were removed and Cr_3Ga_4 and Mn phases were formed. The results and χ^2 parameter that is a criterion of Rietveld refinement are demonstrated in Table 1.

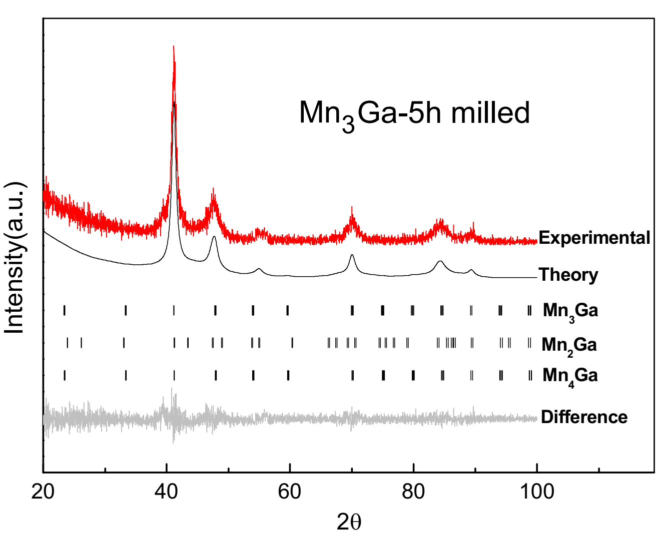

Fig. 1. XRD patterns and Rietveld refinement results of Mn_3Ga synthesized by arc-melting and 15 h milled.

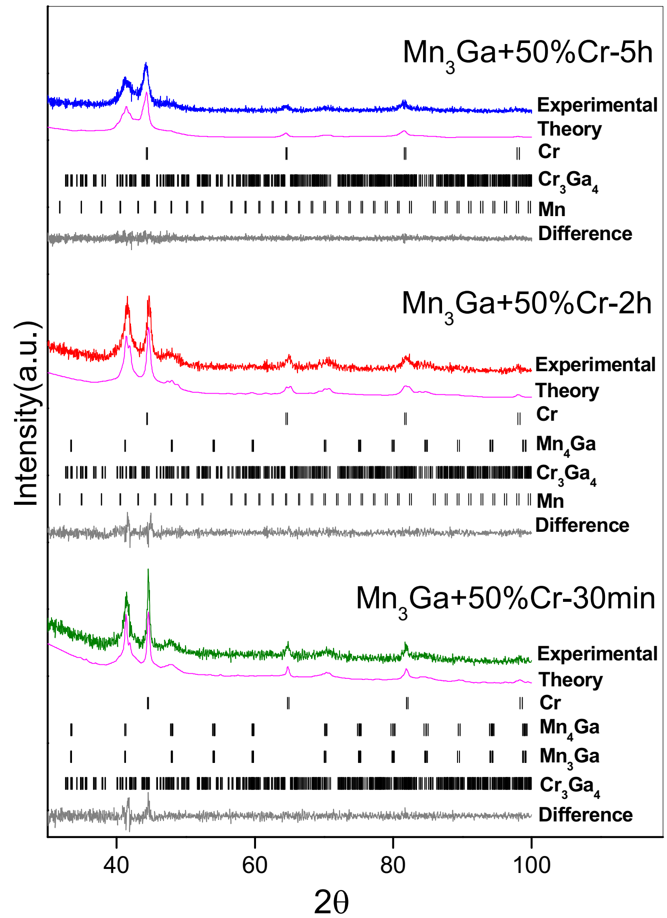

Fig. 2. XRD patterns and Rietveld refinement results of Mn_3Ga-50 wt% Cr synthesized by different milling time.

It has been reported that more than 90% of the mechanical energy imparted to the powders during milling process is transformed into heat [26]. During the collision event, the local temperature increases in a fraction of second. It can be concluded that at the collision point, Ga atoms diffuse from Mn-Ga phase to Cr phase because of the high temperature. Diffusion of Ga atoms to Cr phase is mostly boundary diffusion. This phenomenon occurs at high temperatures and the collision places will rapidly be cooled. Diffusion of Ga atoms from Mn-Ga alloys into the Cr structure results in the formation of Cr_3Ga_4. Cr_3Ga_4 product has a monoclinic structure with C/2 m space group. Cr_3Ga_4 lattice parameters remain approximately constant during ball milling process. Earlier, a same structure was obtained in the high temperatures synthesis of Cr-Ga-M(M=Si,N) ternary system [27,28]. The Néel temperature T_N of the Cr-Ga alloy depends on the concentration of Cr. It indicates the Néel temperature for Cr_3Ga_4 is higher than room temperature [29]. The Cr_3Ga_4 structure is similar to Fe_3Ga_4 [30]. At temperatures above 17 °C, in a weak applied field Fe_3Ga_4 is antiferromagnetic with a Néel temperature of 119 °C [31]. From these results, one supposes that the Cr_3Ga_4 shows a weak antiferromagnetic behavior.

By diffusion process, the amount of Mn increases in the structure. Mn_2Ga and Mn_3Ga changes to Mn_4Ga or Mn phase. Similarly, Mn_4Ga changes to Mn. This process will continue until a full removal of Ga from Mn-Ga structures. Mn has four allotropic forms: