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A new tetragonal phase in CoFeCrGe Heusler alloy

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ABSTRACT

CoFeCrGe ribbons were prepared by melt spinning and then annealed at 300 °C for 4 h and 500 °C for 4 h, respectively. The as-spun ribbons of CoFeCrGe have the B2 type structure with $a = 0.287$ nm. The CoFeCrGe ribbons annealed at 300 °C are composed mainly of the $L2_1$ type structure with $a = 0.578$ nm in partial disorder and the B2 type structure with $a = 0.289$ nm in further disorder case. The ribbons annealed at 500 °C are composed of three compounds with average compositions of $Co_{26.0}Fe_{26.5}Cr_{23.5}Ge_{24.0}$, $Co_{3.8}Fe_{6.4}Cr_{68.5}Ge_{21.3}$ and $Co_{53.4}Fe_{30.4}Cr_{8.6}Ge_{7.6}$, listed in a sequence of volume percentage from major to minor. The primary compound $Co_{26.0}Fe_{26.5}Cr_{23.5}Ge_{24.0}$ is the $L2_1$-type structure with $a = 0.571$ nm in partial disorder and the B2 type structure with $a = 0.286$ nm in further disorder case. The secondary compound $Co_{3.8}Fe_{6.4}Cr_{68.5}Ge_{21.3}$ has a cubic Cr_3Ge structure with $a = 0.461$ nm. The tertiary compound $Co_{53.4}Fe_{30.4}Cr_{8.6}Ge_{7.6}$ is a new tetragonal structure with lattice parameters $a = 0.76$ nm, $c = 0.284$ nm, which were determined by using tilt-series electron diffraction technique in this work. The tertiary (Co, Fe)-rich phase is usually embedded in the matrix of the secondary Cr-rich phase, but there is no special orientation between the two phases. The difference in the magnetic hysteresis loops of the samples annealed at 300 °C and 500 °C has been interpreted as the appearance of the new tetragonal crystalline phase. Element doping is the possible way for further developing the single tetragonal phase or increasing the amount of this phase.

1. Introduction

Magnetic materials in the class of Heusler compounds such as Co_2CrGe, CoFeCrGe are attracting much attention recently for their potential in spintronic devices. Since the electronic band structure of half-metals is metallic for one spin channel and semiconducting or insulating for the opposite spin channel, they are capable of producing spin currents of only one orientation (100% spin-polarized current) [1–7]. Regular Heusler compounds have the X_2YZ elemental composition, where X and Y are the transition-metal elements and Z is the main-group element and crystallize in the cubic $L2_1$ (prototype Cu_2MnAl) structure. This type of compound may deteriorate into the B2 structure when chemical disorder occurs. Further, some of the Heusler compounds crystallize in tetragonal structure with large perpendicular magnetic anisotropy, showing potential for spin-transport torque (STT)-based memory and permanent-magnet applications as well [8,9]. Quaternary Heusler compounds with elemental composition XX'YZ (prototype LiMgPdSn) also exist basically as the derivatives of X_2YZ compounds with one of the X atoms being replaced by another transition-metal element [10].

Experimental and theoretical investigations of two quaternary alloys CoFeCrSi and CoFeCrGe were reported in prior work [7]. In the CoFeCrGe system, the cubic $L2_1$ structure with partial disorder was found in ribbons annealed at low temperature and a phase decomposition was observed when the samples were annealed above 402 °C. The as-spun and 300 °C-annealed CoFeCrGe samples show ferrimagnetic spin order at room temperature and have Curie temperatures (T_C) significantly above room temperature. The measured saturation magnetization, 535 emu/cm^3 (2.8 μ_B/f. u.), is close to the theoretically predicted value of 3.0 μ_B/f. u. for the half-metallic phase. The saturation magnetization is 672 emu/cm^3 for CoFeCrGe ribbons annealed at 500 °C. Powder X-ray diffraction (XRD) analysis confirmed a phase

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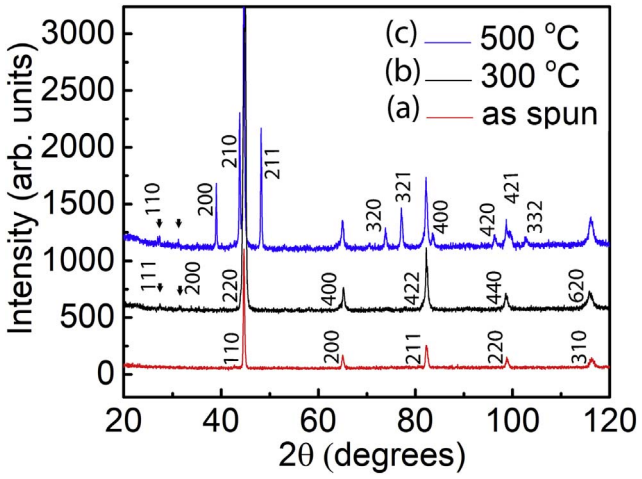

Fig. 1. The XRD diagrams of (a) the as-spun, (b) the 300 °C-annealed and (c) the 500 °C-annealed FeCoCrGe ribbons. The detailed analysis is given in the context. For clarity, the diagrams in (b) and (c) are shifted up, only the indexes of the $L2_1$ structure are labeled in (b) and only the indexes of the Cr-rich (Cr, Fe, Co)$_3$Ge phase are labeled in (c).

decomposition in the 500 °C-annealed CoFeCrGe samples. The diffraction peaks were indexed with two compounds with structural prototypes of Co_2FeGe and Cr_3Ge. However, the rather weak peaks in the XRD diagram of the 500 °C-annealed ribbons cannot be indexed by the $L2_1$ phase or the secondary Cr-rich phases. These suggest the existence of another intermetallic phase in the 500 °C-annealed ribbons.

In the present work, the compositions and structures of the crystalline phases in the annealed samples were systematically characterized by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), selected-area electron diffraction (SAED) and high-resolution electron image (HREM) experiments. The magnetic measurements of the samples annealed at 300 °C and 500 °C in the previous work [7] are reinterpreted with the results of the crystalline phase analysis.

2. Experimental Methods

Ingots of the equiatomic CoFeCrGe alloy were arc melted from high-purity (99.95%) elements in an argon atmosphere. The ribbons about 2 mm-wide and 50 μm-thick were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel with tangential wheel speeds of 25 m/s. Two sets of CoFeCrGe ribbons were annealed under high purity of protective argon at 300 °C for 4 h and 500 °C for 4 h, respectively. The magnetic properties were measured using a SQUID magnetometer with applied magnetic field in the ribbon plane.

TEM specimens were prepared by grinding the ribbons into fine powders in ethanol solution and then put a drop of the liquid mixture onto a Cu grid with C film. TEM experiments were performed with a 200 kV Thermo Fisher Scientific (previous FEI) Tecnai Osiris (scanning) transmission electron microscope equipped with the ChemiSTEM system and Bruker's ESPRIT software. The experimental SAED patterns were analyzed using LANDYNE software [11], e.g., SAED3d [12], QSAED [12] and SPICA [13]. SAED3d was used for simulation and analysis of electron-diffraction patterns, QSAED was used for retreating diffraction intensity and SPICA for generating stereographic projection, applicable to specimen orientation adjustment in TEM experiments.

3. Structural Characterization

Structural properties of as-spun CoFeCrGe ribbons and those annealed at two different temperature are shown in Fig. 1. The powder XRD pattern of the as-spun CoFeCrGe ribbons can be indexed with a compound of B2 structure with $a = 0.287$ nm; the powder XRD pattern of the 300 °C-annealed CoFeCrGe ribbons can be indexed with two phases: the $L2_1$ structure with $a = 0.578$ nm in partial chemical disorder and the B2 structure with $a = 0.289$ nm in further disorder case; the powder XRD pattern of the 500 °C-annealed CoFeCrGe ribbons can be indexed with the multiple phases: the primary compound is the $L2_1$ structure with $a = 0.571$ nm in partial chemical disorder and the B2 structure with $a = 0.286$ nm in further disorder case, and the secondary phase is the Cr-rich (Cr, Fe, Co)$_3$Ge phase with $a = 0.461$ nm. However, the rather weak peaks in the XRD diagram of the 500 °C-annealed ribbons cannot be indexed by the $L2_1$ phase or the secondary Cr-rich phases.

3.1. TEM Study of the Main Compound in CoFeCrGe Alloys

Fig. 2 shows the TEM images of the primary compound in the as-spun, 300 °C-annealed and 500 °C-annealed samples, respectively. The grain size increases from about 10 nm in the as-spun samples to several hundred nm in the 300 °C-annealed samples and decreases to about

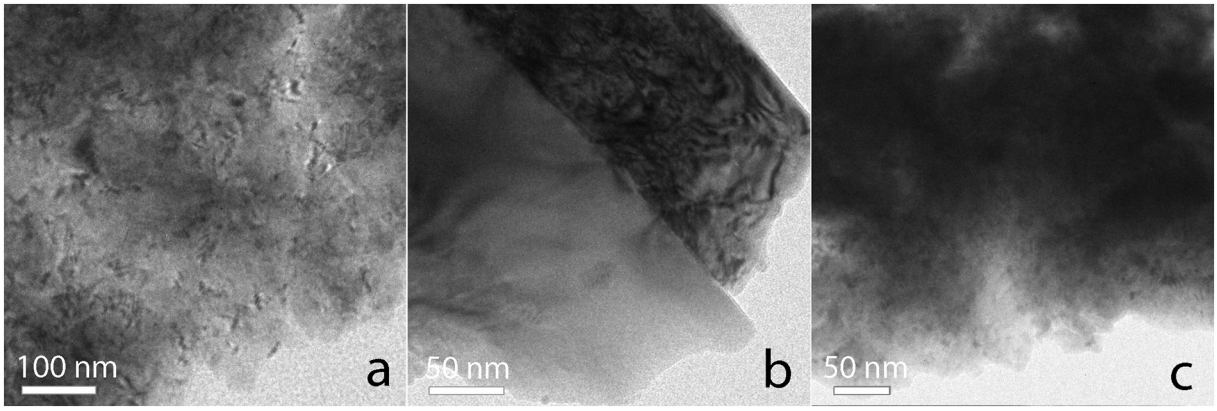

Fig. 2. TEM images of (a) the as-spun, (b) the 300 °C-anneal and (c) the 500 °C-anneal FeCoCrGe ribbons.