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Annealing temperature dependence of crystal structures and magnetic properties of Fe_2CrAl and Fe_2CrGa Heusler alloys

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ABSTRACT

The crystal structures, spontaneous magnetic moment, I_s, and the Curie temperature, T_C, of Fe_2CrAl and Fe_2CrGa Heusler alloys were investigated. Single phases of $A2$, $B2$ and $L2_1$-type structures were obtainable in Fe_2CrAl alloy by controlling the annealing temperature. The values of the I_s and T_C of the $A2$-type phase were 2.2 μ_B/f.u. and 316 K and those of the $B2$-type phase were 2.0 μ_B/f.u. and 274 K, larger than those of the $L2_1$-type phase of 1.6 μ_B/f.u. and 210 K, respectively. A single phase of the $A2$-type phase in Fe_2CrGa alloy was obtained and the I_s and T_C were about 2.8 μ_B/f.u. and 353 K, respectively. The $B2$ or $L2_1$-type single phases of Fe_2CrGa alloy could not be obtained because of the inevitable precipitants.

1. Introduction

Heusler-type ternary alloys have received much attention in the field of materials science because their magnetic and transport properties exhibit a significantly rich variety of behaviors. For example, Fe-based Heusler alloys such as Fe_2VAl and Fe_2VGa have attracted strong attention as intriguing candidates for thermoelectric applications associated with the existence of a pseudo-gap around the Fermi energy (E_F) in their electronic structures, and it has been reported that off-stoichiometric alloys indicate a large Seebeck coefficient [1–3]. For Co-based $L2_1$ Heusler alloys, it has been pointed out that they exhibit half-metallic ferromagnets (HMFs) in their electronic structures from theoretical calculations [4–9]. The HMFs showing a complete (=100%) spin polarization at the E_F are promising candidates for use in tunneling magnetoresistance (TMR) devices, and therefore, many kinds of experimental studies of the magnetic tunneling junctions (MTJ) have been intensively conducted [10–13]. Recently, the theoretical investigations related to the half-metalicity have been extended to Fe-based Heusler alloys, and some of them have been proposed as HMFs in analogy with Co-based Heusler alloys [14–17]. For example, systematic theoretical studies on the electronic structures of the $L2_1$ phase in Fe_2CrZ (Z = IIIb, IVb and Vb elements) Heusler alloys have been reported by Ishida et al. [17], and they showed that complete spin polarization is exhibited when Z = Ge, Sn and Sb. From comparison of the total energy in some assumed chemical disordered states, it has been suggested that the chemical disordering between Fe and Cr may occurs rather than the disordering between Fe and Z. It is well known that the spin polarization of HMFs is often affected by atomic disorder and defects [9,16]. Thus, the investigation of the phase state and phase stability for Fe-based Heusler alloys is very important.

The lattice constant at the room temperature and magnetic data of Fe_2CrAl and Fe_2CrGa alloys reported by co-workers are listed in Table 1 [18–21]. Although there are several reports on Fe_2CrAl Heusler alloy, the resultant data seem to be slightly different from each other. Systematic study for one specimen with different thermal treatments will be needed to clarify the reason for the difference in the magnetic data. In the present study, therefore, the crystal structures and magnetic properties of Fe_2CrAl and Fe_2CrGa Heusler alloys were investigated with specimens annealed at different temperatures.

2. Experimental

Ingots were made by arc-melting in an argon gas atmosphere and annealed at 1573 K for 6 h in the case of Fe_2CrAl alloy or at 1373 K for 3 days in the case of

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Table 1
Reported crystal structure, room temperature lattice constant, a (nm), experimental magnetic moment at 4.2 K, I_s (μ_B/f.u.), the Curie temperature, T_C (K), and annealing condition of the Fe_2CrAl and Fe_2CrGa alloys (WQ: water quench, SC: slow cool) [18–21].

Alloy	Crystal structure	Lattice constant, a (nm)	I_s (μ_B/f.u.)	T_C (K)	Ref.
Fe_2CrAl	$L2_1$	0.5805	1.67	246	[18]
	$B2$	0.287 ($2a$ = 0.574)	1.7	265	1103 K WQ [19]
	$B2$	0.290 ($2a$ = 0.580)	1.75	234	1173 K WQ [20]
	$L2_1$ + fct	0.5811	1.508	348	673 K SC [21]
Fe_2CrGa	$L2_1$	0.5824	2.60		[18]

Fe_2CrGa alloy, with subsequent additional annealing being carried out in various thermal conditions. For Fe_2CrAl, annealing at 873 K for 9 days or at 673 K at 20 days was additionally performed and for Fe_2CrGa, annealing at 873 K for 5 days or at 673 K for 5 days was done. Microstructures were checked with an optical microscope, and the compositions of the specimens were identified with an electron probe micro-analyzer for Fe_2CrAl (Fe: 49.70, Cr: 25.12, Al: 25.18 at.%) and Fe_2CrGa (Fe: 50.56, Cr: 25.51, Ga: 23.93 at.%). Differential scanning calorimetry (DSC) measurements were made with cooling and heating rates of 10 K/min. The crystal structures of the specimens were investigated with X-ray powder diffraction (XRD) using Co Kα or Cu Kα radiation, and electron diffraction (ED) and transmission electron microscopic (TEM) observations. The powdered specimens were annealed again at the same temperature as the final annealing temperature in order to remove the strain, such as 1573 K or 1373 K for 1 min, 873 K for 15 min, or 673 K for 40 min. Thin film specimens for TEM observations were prepared by twin-jet electropolishing in acetic acid and perchloric acid based etchant. All TEM images were taken under 2-beam conditions. Magnetic measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM). The heating rate of the magnetic measurements was 2 K/min.

3. Results and discussion

3.1. Fe_2CrAl alloy

DSC heating and cooling curves of Fe_2CrAl alloy annealed and quenched from 1573 K for 6 h and additionally annealed at 673 K for 20 days are shown in Fig. 1. In the figures, two endothermic peaks can be observed at 818 and 1155 K in the heating DSC curve as indicated by arrows, suggesting the existence of order–disorder phase transitions from the $L2_1$ to the $B2$ phase or from the $B2$ to the $A2$ phase. XRD measurements were carried out for the three kinds of specimens, as-quenched from 1573 K and finally annealed at 873 or 673 K. Fig. 2(a) shows room temperature XRD patterns of Fe_2CrAl and Fig. 2(b) displays the spectra enlarged in the lower 2 theta region. It is determined from these XRD patterns that the specimens annealed at 873 K and 673 K have an $L2_1$-type structure because of the existence of 1 1 1 superlattice reflection, while the crystal structure of the 1573 K specimen is the disordered $A2$-type structure with no ordered reflection. Since the intensities of the superlattice reflections are significantly weak, TEM observations were also carried out.

Fig. 3 indicates ED patterns and TEM dark-field (TEM-DF) images for the Fe_2CrAl alloy annealed and quenched from 1423 K for 1 day, from 873 K for 9 days and from 673 K for 20 days. The ED for the specimens annealed at 873 K clearly indicates superlattice spots for the $B2$-type structure, and no anti-phase domain (APD) boundary is observed in the TEM-DF image taken from 1 0 0 ordered spot. Additionally, the ED pattern for 673 K can be indexed as the $L2_1$-type structure, including 1 1 1 reflection as in the case of the XRD result. From these facts, it can be concluded that the observed peak at 818 K in the DSC heating curve is attributed to the order–disorder phase transition from the $L2_1$ to the $B2$ phase. The value of the determined transition temperature, $T_t^{L2_1/B2}$, is comparable to that (about 820 K) from $D0_3$ to the $B2$ phase in the binary Fe_3Al alloy [22,23], and this

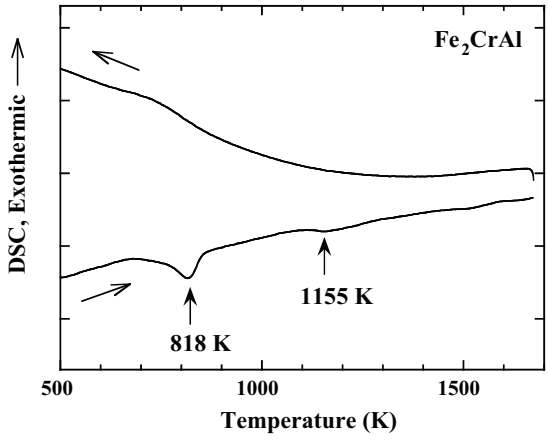

Fig. 1. DSC heating and cooling curves of Fe_2CrAl alloy finally annealed at 673 K for 20 days.

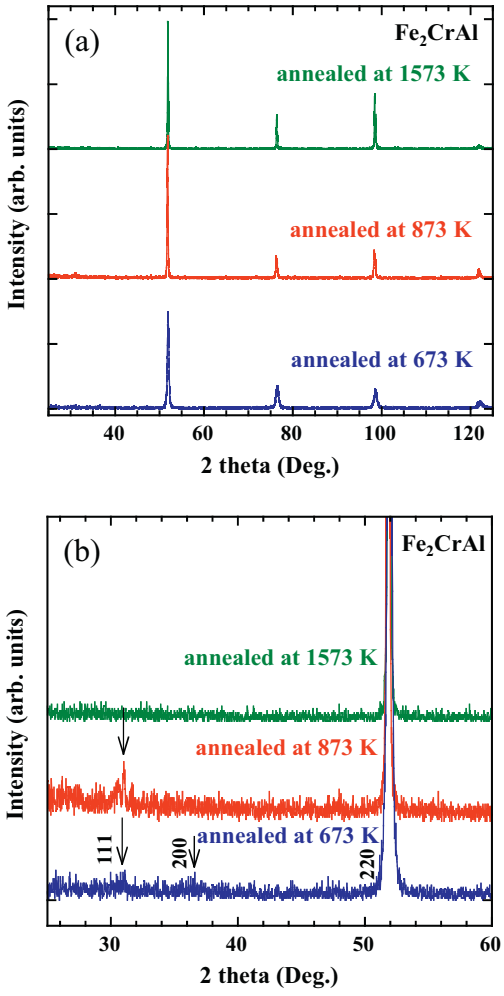

Fig. 2. (a) Room temperature X-ray powder diffraction patterns of Fe_2CrAl alloy annealed and quenched from 1573, 873 and 673 K measured with Co Kα radiation. (b) Enlarged scale in the lower 2 theta region.