Ab-initio Calculation of Structural and Magnetic Properties of Annealed Cu_2MnAl Heusler Alloy

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Abstract. Heusler alloys attracted considerable interest for their versatile magnetic properties. In this paper, Cu_2MnAl Heusler Alloy samples were prepared with high vacuum melting furnace under the atmosphere of pure Argon. Then the samples were crushed and milled by planetary miller to get a uniform grading about 2 to 3 um thick. The milled powders were annealed under a mixed controlled atmosphere of pure Hydrogen and pure Nitrogen at different temperatures. The treated powders were characterized by X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). The structural property of Cu_2MnAl was calculated by ab-initio method. Different types of refined structures of Cu_2MnAl with different element occupation ratios and different occupation sites were calculated and the XRD patterns of the corresponding structures were concluded. With the calculated results, the property of the annealed powers of Cu_2MnAl was demonstrated. The Cu_2MnAl achieved its maximum saturation magnetization (Ms) of 72emu/g and minimum coercive (Hc) at 200℃ annealing temperature with $L2_1$ ordered structure. Other phases like Al_2Mn_3 and Cu_9Al_4 were formed when annealed above 300℃, and the Ms of the material drops between 200℃ and 400℃ or above 700℃, but rises between 400℃ and 700℃with its crystallization increased.

Introduction

Heusler alloys has attracted considerable interest for their versatile magnetic properties and their potential in spin electronics [1]. The majority of the Heusler alloys are ferromagnetic and can saturate in weak applied magnetic fields. The magnetic properties of Heusler alloys are determined by their crystal structures, composition and heat treatment. The Cu_2MnAl Heusler alloy is a typical full-Heusler alloy. In this paper, we use high frequency induction furnace to synthesis the material. Then heat treated the samples in different protective atmosphere at different temperature to get the best crystalline samples [2]. The static magnetic properties of the samples were tested. By using Ab-initio method the structure of Cu_2MnAl were optimized and simulated. Both the total and the individual magnetic moments of the atoms were calculated [4]. Then the crystal phases appeared in the heat treatment process were analyzed and calculated.

The Heusler alloys have localized magnetic properties and are ideal model systems for studying the effects of both atomic disorder and changes in the electron concentration on magnetic properties.

Sample Preparation and Experimental Procedures

The samples were prepared by melting pure elements in high frequency induction furnace in argon ambience to prevent oxidation and vaporization.

The rough structural characterization of the samples were analyzed by X-ray diffractometer. The experimental conditions and parameters were kept identical for all the samples to ensure convincing results.

The magnetic properties of the samples were measured by vibrating sample magnetometer (VSM) at 2K and 293K in a field up to 5T.

The samples were annealed under a mixed controlled atmosphere of pure Hydrogen and pure Nitrogen at different temperatures. The structures of the annealed samples were measured by XRD. The dynamic magnetic parameters were measured by Vector Network Analyzer (VNA).

In the meantime, the basic properties of Cu_2MnAl were calculated through First-Principle method. The lattice constant, the theoretical structure, the atomic magnetic moment were obtained. Also the calculation of the crystal phases appeared in the heat treatment process were carried out.

Results and Discussion

Magnetization and X-Ray Spectrum Analysis

We tried vacuum annealing and annealing under pure N_2. But the samples are chemical active and were easily oxidized. The oxidized sample had no metallic luster and had poor magnetic performance. So we added 30% of H_2 into the protective atmosphere of the annealing process. Due to the strong reducibility of hydrogen, the oxidation were eliminated. The results were much better.

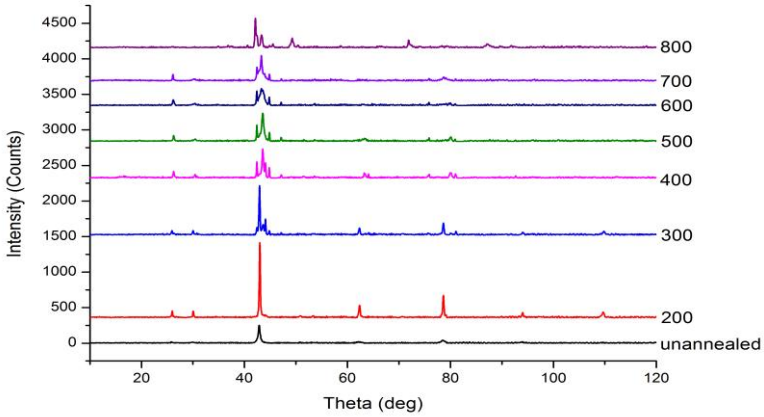

Fig.1 XRD spectrum of annealed Cu_2MnAl at different temperature

From the X-Ray Diffraction spectrum, the crystalline structure of the Cu_2MnAl samples are revealed. The unannealed samples are low in crystallinity. The heat treated samples were transformed into crystalline state.

The following figures showed the hysteresis loops of the samples after annealing in mixture of H_2 and N_2.

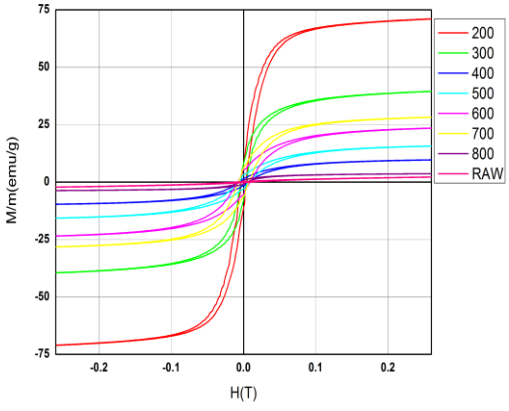

Fig.2 Hysteresis loops at 293K

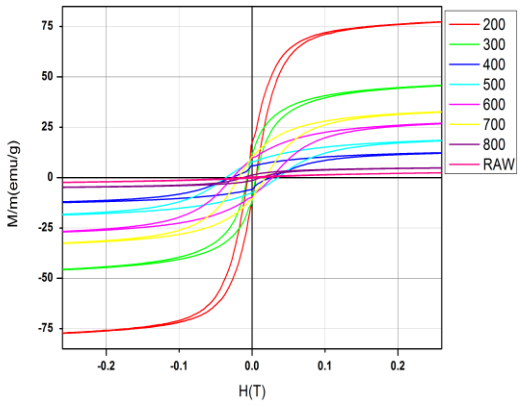

Fig.3 Hysteresis loops at 2K

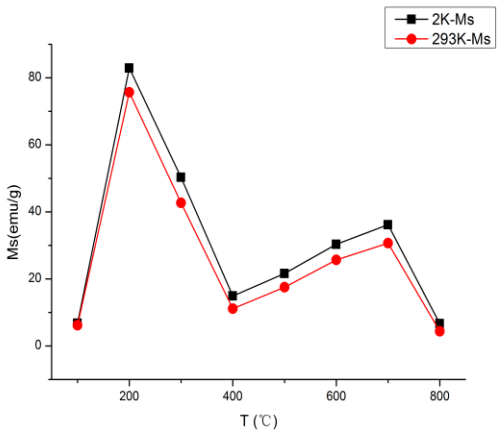

Fig.4 Ms at different annealing temperature

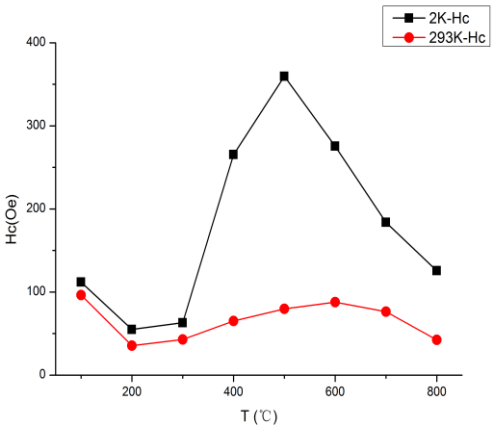

Fig.5 Hc at different annealing temperature

Before the heat treatment process, the saturation magnetization of the Cu_2MnAl can hardly be reached. Even at a strong magnetic field of 5T, the value did not show any trend of saturation. But after the heat treatment process, the samples easily reached its saturation magnetization at a much weaker magnetic field of 2T.

The saturation magnetization of the annealed Cu_2MnAl samples decreased when temperature rising from 200 to 400, but increased when temperature continued to rise from 400 to 700. When the annealing temperature exceeded 700 degrees, the magnetic property of the samples drops dramatically to a much lower level.

From the XRD spectrum, The samples annealed at 200℃ had the best crystalline structure and the highest crystallinity. As a result the saturation magnetization was the highest of all the samples. The crystallinity of the samples annealed above 200℃ decreased as the peaks turned wide and new peaks of crystalline phase were formed. From 200℃ to 400℃, the formation of the new crystalline phase and the destruction of the Heusler phase was the predominant factor. So the saturation magnetization of the samples dropped. From 400℃ to 700℃, the grain size increased as the annealing temperature rising was the predominant factor, leading to the rise of the saturation magnetization. When annealing above 700℃, the Heusler phase was almost completely destroyed. So the saturation magnetization dropped substantially.

Ab-initio Calculation on Cu_2MnAl

The full-Heusler alloys possesses the $L2_1$ structure and Fm-3m space group. With this neat crystal structure, the structural properties and the magnetic properties of the material can be calculated by ab-initio calculations.

In this paper, we use Vienna Ab-initio Simulation Package (VASP) and Material Studio to perform the calculations.The structure of the Cu_2MnAl alloy was built as shown in Fig.6.

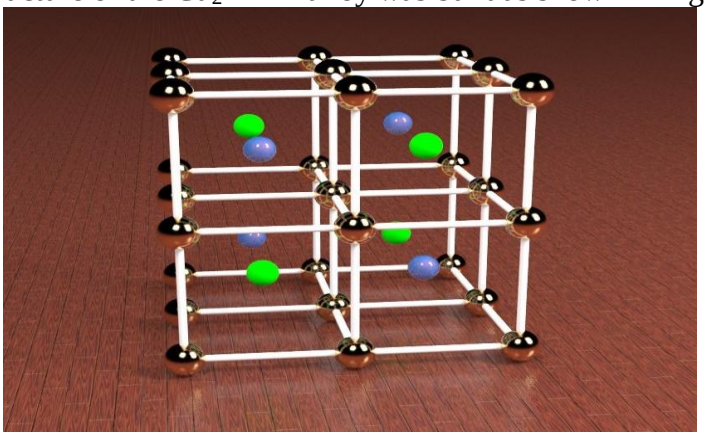

Fig.6 $L2_1$ Structure of Cu_2MnAl(Blue for Mn; Green for Al; Golden for Cu)

First the geometry optimization calculation was performed. By changing the lattice constant and the relaxation of the atomic site occupation, the energy of the models with different parameters were calculated. The result was show in the figure below. By using the curve-fitting method, the minimum energy of the models can be found whose corresponding lattice constant is the theoretical calculation result.

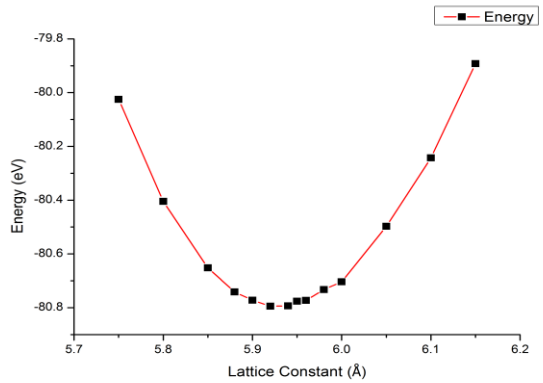

Fig.7 Energy of models with different lattice constant

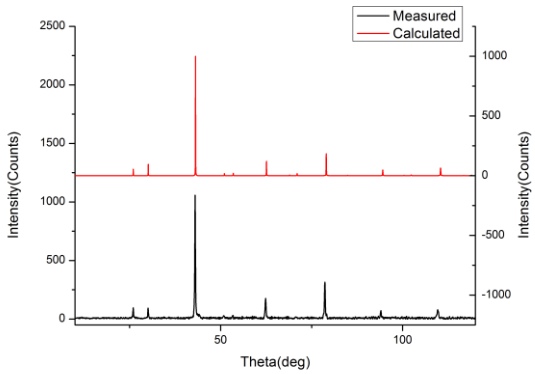

Fig.8 Measured and Calculated XRD spectrum of Cu_2MnAl

The results were drawn in Fig.7, the relation between the lattice constant and the total energy of the models were fitted by polynomial method. The lowest point of the fitting curve corresponded the model with minimum energy. Its corresponding lattice constant was the calculated result. The result was A=5.931Å.

Use the calculated lattice constant, the theoretical structure of the Cu_2MnAl $L2_1$ structure can be built. By using the powder diffraction method, the theoretical XRD spectrum can be simulated.

The following figure shows the XRD spectrum of the calculated theoretical result and the 200℃ annealed sample. These two spectrum are identical to each other which proves the validity of the theory and the accuracy of the experiment.

By comparing the theoretical XRD spectrum and the experimental testing result, the specific structure of the material can be analyzed, isolated and explained.

The simulation of the $L2_1$ structure was identical to the 200℃ annealed samples which had the best magnetic performance.

When annealing above 200℃, other phase as Al_2Mn_3, Cu_9Al_4 appeared. Annealing above 700℃ the original $L2_1$ structure was almost completely destroyed.

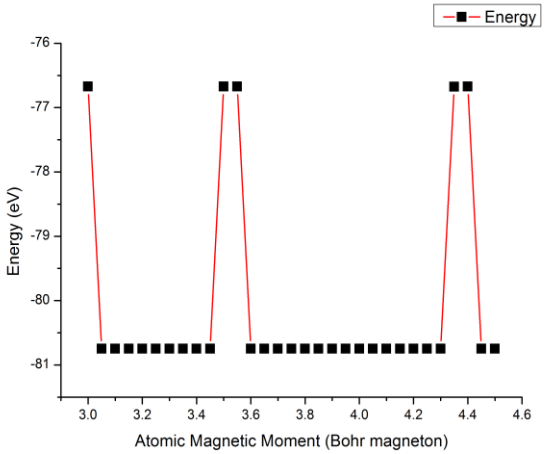

Fig.9 Energy of models with different initial atomic magnetic moment of Mn

Then the magnetic property of the model could be calculated by VASP.

By assigning different initial value of the atomic magnetic moment of Mn atoms, the energy of the system converged when the initial value was in a certain interval. And such initial values leaded the individual atomic magnetic moment of the elements to converge to a certain point as well.

Tab.1 Magnetic moments of atoms

Element	Al	Mn	Cu	total
Atomic magnetic Moment	-0.036[μ_B]	3.324[μ_B]	0.053[μ_B]	13.576[μ_B]

The result showed the total magnetization of the $L2_1$ structure cell is 13.576μ_B. The atomic magnetic moment of the Mn atom is 3.324μ_B.

By analyzing the XRD spectrum of the annealed samples, we found that Al_2Mn_3 and Cu_9Al_4 appeared when annealing above 300℃. So we made model structure of Al_2Mn_3 and Cu_9Al_4, and calculated the atomic magnetic moment of each.

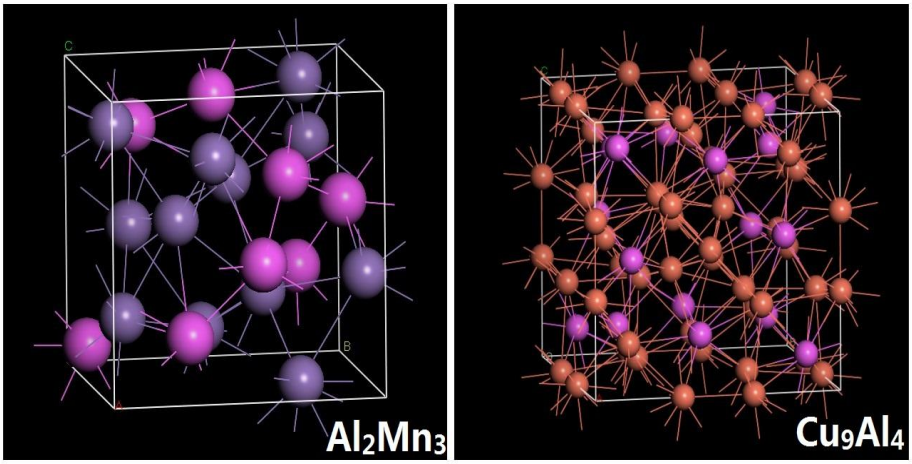

Fig.10 Structure of Al_2Mn_3 and Cu_9Al_4

Then we simulated the XRD spectrum of these two structures. And they matched with the experimental samples.

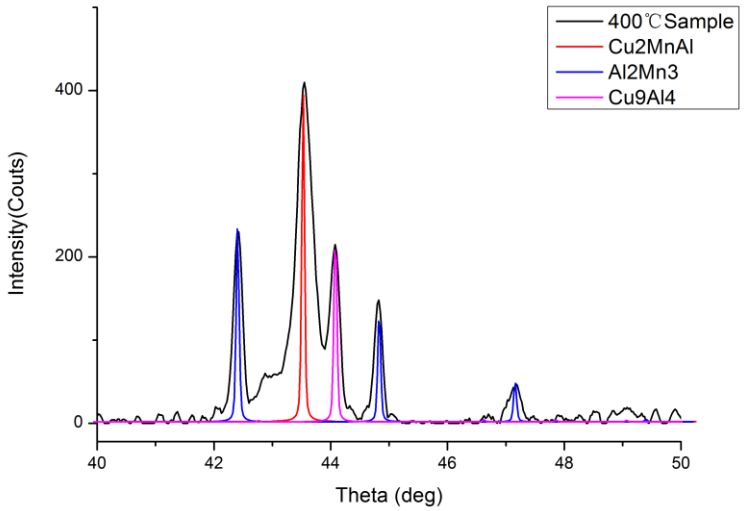

Fig.11 Crystal phases found in 400℃ annealing sample

Then we calculated the atomic magnetic moment of Al_2Mn_3 and Cu_9Al_4.

Tab.2 Magnetic moments of atoms

Element	Al	Mn	Cu	total	Num of Mn
Cu_2MnAl	-0.036[μ_B]	3.324[μ_B]	0.053[μ_B]	13.576[μ_B]	4
Al_2Mn_3	-0.056[μ_B]	1.838[μ_B]	X	21.601[μ_B]	12
Cu_9Al_4	0	X	0	0	0

The result was clear and convincing. Cu_9Al_4 possesses no magnetic moment, the Mn atom in Al_2Mn_3 possesses less atomic magnetic moment than it in Cu_2MnAl.

When the annealing temperature was above 300℃, the generation of Al_2Mn_3 and Cu_9Al_4 brought down the total Ms of the samples. But as the annealing temperature kept rising from 400 to 700℃, Cu_9Al_4 began to disappear and Cu_9Al_4 was transformed into Al_2Mn_3 and Cu_2MnAl. So the total Ms of the samples slowly increased. When the annealing temperature reached 800℃, Cu_2MnAl was not left. So the total Ms dropped to a very low level.

Conclusion

In this paper, we use both the theoretical simulation method and the experimental method to research the magnetic properties of Cu_2MnAl Heusler alloy. The results of two methods mutually reinforcing one another. And the precise XRD spectrum was obtained. The Ms of the sample reached 82.88emu/g at 2K. The sample with higher ordered structure had the higher Ms and lower Hc. The total magnetic moment of the Cu_2MnAl primitive cell is 13.576μ_B. Each Mn atom generates 3.324μ_B. The samples of Cu_2MnAl reached its best $L2_1$ crystal structure when annealing at 200℃. When the annealing temperature increased, phases like Al_2Mn_3 and Cu_9Al_4 with less magnetic moment were formed. So the static magnetic properties of the samples deteriorated. The difference of material performance were explained by the change of crystalline phases.

References

[1] Leonid Sandratskii, Peter Dederichs, Olle Eriksson. First-principles study of the exchange interactions and Curie temperature in Heusler alloys. Halle, 34-45(2006).

[2] Denise Erb, Gregor Nowak, Kurt Westerholt. Thin films of the Heusler alloys Cu_2MnAl and Co_2MnSi: recovery of ferromagnetism via solid state crystallization from the x-ray amorphous state. Journal of Physics D: Applied Physics, 43,285001:1-9(2010)

[3] M. Obaida, K. Westerholt, H. Zabel. Magnetotransport properties of Cu_2MnAl, Co2MnGe and Co2MnSi Heusler alloy thin films: From nanocrystalline disordered state to long-range-ordered crystalline state. Physical Review B,84,184416,(2011).

[4] S. Picozzi, A. Continenza. Co_2MnX(X=Si, Ge, Sn) Heusler compounds: An ab initio study of their structural, electronic and magnetic properties at zero and elevated pressure. Physical Review B, 66, 094421, (2002).

[5] Jia Li, Yangxian Li, Guoxiang Zhou. A first principles study on the full-Heusler compound Cr2MnAl. Applied Physics Letters,94,242502, (2009).

[6] H. Rached, D. Rached, R. Khenata. First-principles calculations of structural, elastic and electronic properties of NiMnZ (Z = Al, Ga and In) Heusler alloys. Phys. Status Solidi B, 246, No. 7:1580–1586,(2009).