ORIGINAL RESEARCH ARTICLE

(GdxDy1-x) 12Co7 Magneto-thermal Effect

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ABSTRACT

Because of its own advantages such as energy saving and environmental protection, the greenhouse magnetic refrigeration technology is attracting more and more attention. Magnetic refrigeration materials as one of the key technology, its development has a very important role. This paper begins with a brief overview of the basic principles of magnetic refrigeration and the development of magnetic refrigeration materials. In this paper, the phase structure and Magnetocaloric effect of (GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series alloys were investigated by X-ray diffraction and magnetic properties measurements. The results show that all samples are monoclinic crystals, with the Gd composition increases, the Curie temperature of the alloy from 92K to 142K linear increase. In the case of an external magnetic field of 2Td, the maximum magnetic entropy of the (GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series alloy becomes 6.93 J / kg · K. By analyzing the XRD patterns of the alloys and the graphs of the M-H and Arrott graphs, it is shown that the alloy is transformed from a secondary phase transition to a primary phase transition.

KEYWORDS: (GdxDy1-x) 12Co7 system; Magnetic entropy change; Magnetocaloric effect

1. Preface

1.1. Introduction

Traditional gas compression refrigeration technology has been widely used in the field of household appliances, industrial production, aerospace, defense, geophysical exploration and other fields. However, in recent years it has been found that the refrigerant Freon used in gas refrigeration is not only low in cooling efficiency, but also pollutes the environment and seriously destroys the ozone layer and even brings the greenhouse effect. So the international ban on the use of freon calls more and more intense. On the one hand, people began to actively develop new non-destructive atmospheric ozone layer of gas refrigerant to replace the freon products [1]. On the other hand, people are looking forward to the scientists to bring a new refrigeration technology, mainly non-compressed refrigeration technology, including absorption refrigeration, semiconductor refrigeration and magnetic refrigeration. Magnetic refrigeration is the use of magnetic refrigeration material magnetic thermal effect (that is, in the isothermal magnetization to the outside heat, while the demagnetization of external heat absorption) to achieve the purpose of cooling. Compared with the traditional gas compression refrigeration, magnetic refrigeration with solid magnetic materials as working fluid, do not use Freon and compressor, high cooling efficiency, low energy consumption, less moving parts, low noise, small size, high reliability and no environmental pollution, So the magnetic refrigeration technology experts recognized as high-tech green refrigeration technology. Can replace the traditional gas compression refrigeration technology is widely used in household appliances, industrial production, aerospace, defense and other fields. Therefore, magnetic refrigeration technology is energy efficient and no environmental pollution, the two prominent advantages of the world's researchers and the attention of the attention. Scientists generally believe that room temperature magnetic refrigeration technology has great prospects for development.

1.2. The basic concept of magnetic refrigeration

1.2.1 Magnetocaloric effect

Magnetic thermal effect is inherent in the magnetic material itself, it refers to the magnetic material in the magnetic field changes, the material itself produced by the temperature rise and decrease [2].

1.2.2 Magnetic refrigeration principle

Magnetic refrigeration is the magnetic effect of magnetic materials to cool the new refrigeration technology. The magnetic substance is a crystal composed of protons or magnetic ions with magnetic moments, which have a certain thermal or thermal vibration. When the magnetic field is not applied, the orientation of the magnetic moments in the magnetic matter is irregular (random), and the corresponding entropy is large. The magneto-thermal effect is related to the magnetic entropy change. When the magnetic refrigeration material (paramagnetic material or soft ferromagnetic material) is magnetized, the magnetic moment is preferred in the magnetization direction. Under isothermal conditions, the order of the spin increases. When the magnetic field strength is weakened, the magnetic moment tends to be disordered due to the thermal motion of the magnetic atoms or ions. Under isothermal conditions, the magnetic masses absorb heat from the outside, and the temperature decreases [3].

The principle of paramagnetic and ferromagnetic cooling is basically the same, but the use of ferromagnetic at room temperature is difficult, because paramagnetic is no longer applicable at room temperature. Demagnetization process is actually the process of increasing the magnetic entropy, when the working material in a state of adiabatic, magnetic system energy depends on the rise of lattice thermal energy to compensate for the reduction. Therefore, the smaller the lattice specific heat, the greater the demagnetization temperature drop available. At low temperatures, the Paraelectric lattice has a small specific heat of heat, and it is easy to obtain a large demagnetization temperature drop. However, near room temperature, Paraelectric lattice specific heat increases, only a small temperature drop.

In addition, near room temperature, paramagnetic thermal entanglement energy increased to 70 times the low temperature, then want to discharge the same proportion of magnetic entropy, the required field even if the use of superconducting objects are usually only about 10T Outfield. Therefore, the cis-magnetization is not suitable as a working material for room temperature magnetic refrigeration [4].

While the ferromagnetic material of the magnetic atoms and paramagnetic materials, have a net magnetic moment. The difference is that there is an exchange interaction between adjacent atomic electrons in the ferromagnetic material. But the ferromagnetic is in the field, its spin magnetic moment is actually affected by the external field and the exchange of additional field interaction. The exchange of additional field can be up to several hundred Tesla, which makes the use of Ferromagnets to achieve room temperature magnetic refrigeration is possible, so the room temperature conditions often use ferromagnetic as a magnetic cooling material.

1.2.3 The process of magnetic refrigeration implementation

Understand the basic principles of magnetic refrigeration, the purpose is to achieve magnetic refrigeration.

(1) The role of external magnetization in the magnetic working fluid, the magnetic flux of the working fluid decreases, the temperature rise.

(2) Through the heat exchange of the magnetic mass of heat away.

(3) EBay magnetic field, magnetic work within the optional system has become disorder, in the demagnetization process consumption of energy, so that the magnetic medium temperature drop.

(4) Through the heat exchange of magnetic refrigerant from the low temperature heat pump heat absorption, in order to achieve the purpose of refrigeration [5].

1.3. Thermal and mechanical basis of magnetism

The entropy S (T, H) of the magnet under normal pressure is a function of the magnetic field strength (H) and the absolute temperature (T). She is magnetic entropy SM, lattice entropy SL and electron entropy SE. which is:

$S(T, H) = SM(T, H) + SL(T, H) + SE(T, H)$

The entropy of the ferromagnetic material is the sum of the magnetic entropy and the non-magnetic entropy corresponding to the two permanent magnetic fields (zero magnetic field H0 and non-zero magnetic field H1). The MCE phenomenon (ie, the adiabatic temperature rise Δ Tad (T) ΔH = (T1-T) is observed when the magnetic field applied is H0 and H1 in the adiabatic state (ie, the total entropy in the system remains constant when the magnetic field changes) T0)).

The value of MCE can also be expressed as isothermal magnetic entropy change, in this case, equal to the corresponding S (T) H in the isothermal state. SM (T) == [S01 (T0) - Si (Hi)]. Therefore, the magnetic thermal characteristics can be expressed by the amount of? Tad (T)? H and? SM (T). Tad (T) H and SM (T) H are the functions of the original temperature TU (ie, the temperature before the magnetic field transition) and the magnetic field change (H = H1-H0).

From the thermodynamic point of view, the magnetocaloric effect is through an external force (magnetic field), so that changes in entropy, which further form a temperature change. Derivation of T, SM with thermodynamics, and the derivation process is as follows:

Magnetic material in the magnetic field from the temperature of T for the T pressure of P (Note: because the magnetic material is solid, such as the neglect of thermal expansion, for the sake of simplicity, can be considered constant pressure, that is, regardless of the impact of pressure P)

The differential of the Gibbs function of the system can be obtained

Magnetic entropy

$$S(T, H) = -\left(\frac{\partial G}{\partial T}\right)_H \qquad (1\text{-}2)$$

Magnetization

$$M(T, H) = -\left(\frac{\partial G}{\partial H}\right)_T \qquad (1\text{-}3)$$

Full differentiation of entropy

$$DS = \left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH \qquad (1\text{-}4)$$

Under the constant magnetization field, the magnetic specific heat CH (the specific heat of the material under the magnetization field is defined)

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H \qquad (1\text{-}5)$$

By the equation (1-2), (1-3) available

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \qquad (1\text{-}6)$$

(1-6) is known as the Maxcall relation, and the formulas (1-5) and (1-6) are substituted into (1-4)

$$DS = \left(\frac{C_H}{T}\right)_H dT + \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1\text{-}7)$$

For equations (1-7)

1) under isothermal conditions, dT = 0 ds = $\left(\frac{\partial M}{\partial T}\right)_H dH$ (1-8)

For the integral (1-8) points can be obtained magnetic entropy change SM

$$S_M (T, H) = S_M (T, H) - S_M (T, H = 0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1\text{-}9)$$

2) adiabatic conditions, dS = 0,

$$DT = - \frac{T}{C_H} \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1\text{-}10)$$

Points can be obtained Tad.

3) and other magnetic field conditions, dH = 0,

$$DS = \frac{C_H}{T} dT \qquad (1\text{-}11)$$

Tad, S_M [6] can be obtained according to the equations (1-9), (1-10) and (1-11) by experimentally measuring M (T, H) and CH (H, T) The

1.4. Measurement method of magnetocaloric effect

1.4.1 Direct measurement method

When the magnetic field changes, the magnetic material produces a magnetocaloric effect, the material will produce temperature changes, if the material in the magnetic field before the temperature is recorded as T1, the magnetic field after the end of the temperature recorded as TF, then the material thermal effect T = TF-T. The task of the direct measurement method is to measure the adiabatic temperature change of the magnetic material during the magnetic field change.

Direct measurement device according to the thermometer temperature measurement methods can be divided into direct contact and non-direct contact. The magnets in the direct measuring device can be made of superconducting magnets, conventional solenoid, electromagnets and permanent magnets. According to the different magnets, direct measurement device can be divided into superconducting and often guided.

When measuring the magnetocaloric effect, the magnetic field can be applied directly to the sample or the magnetic field can be removed, or the sample can be directly magnetized or demagnetized by moving the sample into or out of a uniform magnetic field. This method of operation is generally only used for permanent magnet magnetic field, the use of high magnetic field strength is very difficult.

The accuracy of the direct measurement depends on the error of the thermometer, the setting of the magnetic field, the adiabatic condition of the specimen (which is one of the major sources of measurement error when the material MCE is large), and how to compensate for the change in the magnetic field The influence of the thermometer reading. In general, the error is between 5-10%. Since the temperature change of the material is not only affected by the frequency of the magnetic field, but also a function of time, the sensitivity of the temperature sensor is also a very important source of error.

1.4.2 Indirect measurement method

The direct measurement method can only measure the adiabatic temperature change, and the indirect measurement method can not only obtain the SM. You can also get Tad. (2) The heat capacity CH change of the material to calculate SM (T) and Tad (T). (2) Calculate the heat capacity CH of the material to calculate SM (T) and Tad (T).

By comparison, the above three measurement methods have their own advantages and disadvantages. Direct measurement method intuitive but the error is large, difficult to operate. With the measurement of magnetization curve indirectly measured SM method, take a short time, the measurement is relatively simple. Although SM and Tad can be obtained simultaneously by measuring the heat capacity, it takes a lot of time to measure the specific heat of the magnetic field, and the magnetic entropy S [7] is also considered.

1.5. The research program, the main research content, the key issues to be solved and the

technical route

1.5.1 Main research contents

The magnetocaloric effect of (GdxDy1-x) 12Co7 alloy was determined by experimental means, and the micro-related properties were improved by adding trace and other related elements.

1.5.2 Key issues to be addressed

(1) With high vacuum arc furnace in the high purity argon under the protection of molten alloy and quartz glass tube in the annealing of the alloy to solve the problem of easy oxidation of rare earth alloys;

(2) When the rare earth metal is added properly, the chemical composition deviation of the alloy due to melting volatilization is solved by X-ray analysis; the uniformity treatment temperature and time are strictly controlled to solve the problem of uniformity and balance in the alloy.

1.5.3 Research methods and test programs

(1) In the reference of the relevant binary alloy phase diagram and the literature under the premise of a prepared preparation of alloy samples, and the use of high vacuum arc furnace in the high purity argon under the protection of alloy samples;

(2) Determination of representative binary or ternary alloy sample differential thermal analysis data for the development of appropriate homogenization process;

(3) After the milling and desorption annealing, the X - ray diffractometer was used to scan the diffraction data, and the phase analysis was carried out. The phase of each alloy sample was determined by metallographic analysis and electron microscopy analysis.

(4) The MH and MT curves of the compounds studied were determined by vibrating sample magnetometer with low temperature control, constant temperature device and strong magnetic field. The parameters such as the Curie temperature, magnetic entropy change and magnetic susceptibility were obtained by computer program processing. The magnetocaloric properties of the alloy were analyzed.

(5) Combined with experimental data through theoretical analysis, explain the mechanism of alloy performance.

1.5.4 Technical route:

Alloy sample composition → vacuum arc furnace smelting alloy sample → homogenization heat treatment → preparation of appropriate samples → X-ray diffraction analysis, metallographic microscope analysis → phase → select the alloy compound for magnetic thermal effect measurement → the use of tool software data To analyze.

2. Experimental design and test methods

2.1. Ingredients and equipment used

2.1.1 Raw materials

The purity of the raw materials used in this experiment is as follows:

Gd: 99.9% Dy99.9% Co99.9%

2.1.2 Equipment used in this experiment:

Sample smelting using high-frequency induction furnace and non-consumable electric arc furnace

Weighing equipment for the photoelectric analysis of the balance (the amount of 0.1g)

The analytical instrument is an X-ray diffractometer

Lake shore7410 vibration sample magnetometer

2.2. 2.2 Experimental process

2.2.1 Weigh the sample

The content of various components (mass percentage) was calculated based on the conversion of atomic percentages and mass percentages. The quality of the various components contained in each sample was weighed using a photoelectric analytical balance. The quality of each sample is 2 grams.

2.2.2 Smelting samples

Smelting by the Chinese Academy of Sciences Branch of the WK-1 non-consumable vacuum arc furnace is in the high-purity argon gas protection, water-cooled crucible. Before melting, the arc furnace should be vacuumed to reach 10-3 Pa after the range of pure Ar, and then vacuum, to 10-3 Pa and then filled with pure Ar, and the furnace inside and outside the air pressure to protect the sample Not subject to oxidation. The arc current and smelting current during melting are as low as possible to reduce the volatilization loss of the sample (mainly Dy and Gd) during the smelting process, while at the same time ensuring smelting through the sample. To achieve the composition of the alloy evenly, melt again after the need to flip the sample and then melt, so repeated three to four times, so that the melting of the sample composition tends to be uniform, the sample surface smooth and metallic luster. At the same time to ensure that the quality of the sample before and after smelting 1% deviation for the smear before and after the deviation is too large need to re-plaster remover until the deviation is less than 1%.

2.2.3 Homogenization treatment

The melted samples were placed in the porcelain plate in sequence and separated from each sample by asbestos, sealed into a quartz tube, and the quartz tube was evacuated and placed in an annealing furnace. The appropriate annealing time and annealing temperature are selected according to the information provided by the known binary phase diagram. Set the program to sample the homogenization process. The sample is at 600. C annealing, annealing time is 1 day.

2.2.4 Quenching treatment

In order to maintain the organization at high temperatures, after the annealed sample is removed from the annealing furnace, the quartz tube is rapidly quenched into the ice water mixture.

2.2.5 Preparation of powder samples

After homogenization of the heat treatment of the block alloy sample, use coarse sandpaper to remove the surface of the oxide layer, and then under the protection of acetone, in the agate bowl crushed into a particle size of not more than 30 nm powder. Part of the system of the sample brittle relatively large, it is easy to directly crushed grinding. It is generally not due to cold processing grinding and produces significant internal stress. It can be directly X-ray diffraction analysis. However, the rich and rich rare earth alloy samples because of its toughness and ductility is good, it is difficult to use a bowl of ground into a powder, need to file into a fine file [8].

2.2.6 X-ray diffraction

The prepared sample powder was filled into a recessed glass sheet. The X-ray diffraction pattern of the sample was obtained by data collection using a RigakuD / Max 2500V X-ray powder diffractometer. [9] The diffraction condition of the diffractometer is: tube pressure 40KV, pipe flow 200mA, step length 80 / min, scanning range 2θ: 20º-60º. The resulting data were analyzed using the Jade 5.0 program and the powder diffraction database (PDF 2002) to determine the phase composition of each sample.

2.2.7 Optical microscopy analysis

Will be a small piece of alloy samples embedded in the bakelite powder, and sandpaper to sample a plane, and then choose from coarse to fine different models of sandpaper (400 # -2000 # water sandpaper), the sample surface in the metallographic Rough grinding machine. Finally, polished with a Al2O3 polishing agent on the polishing instrument, washed with water, dry. The polished sample was etched with 1% HN03-C2H5OH solution, washed with water and dried. Then use the German LeilaDMRE microscope to shoot metallographic photographs, and select the appropriate magnification.

2.2.8 Lake Shore7410 vibration sample magnetometer

The sample is placed in a single magnetic field and is induced by a magnetic moment. And the sample is placed in the picking coil of the vibrating sample magnetometer, for sinusoidal vibration, the voltage signal is induced in the detection coil due to the change of the magnetic flux through the sample. The signal is proportional to the magnetic moment, so the vibrating sample magnetometer can be used to measure the magnetic properties of the material. The magnetic field can be generated by the electromagnet or superconducting magnet, so the magnetic moment and the magnetization can be measured as parameters of the magnetic field.

As a parameter of temperature, VSM system with superconducting magnet or VSM system with low temperature Dewar electromagnet can be used at lower than normal temperature. Above normal temperature, the VSM system with a heating furnace is available. Because the choice of ferromagnetic materials, mainly depends on their magnetization and hysteresis loop, so VSM system commonly used function is to measure the magnetic properties of ferromagnetic materials [10].

Figure 1. Lake shore7410 vibration sample magnetometer

2.3. Determination of magnetic thermal effect

The main parameters that characterize the magnetocaloric properties of a magnetic refrigeration material are the magnetic ordering temperature (for ferromagnetic materials, called the Curie point) and the magnetic thermal effect at the corresponding temperature (generally using a magnetic field change The magnetic entropy change SM of the magnetic refrigeration material and the adiabatic magnetization temperature change ΔT). Magnetic entropy change SM, adiabatic magnetization temperature T test calculation principle has been mentioned in the first chapter. Magnetic thermal test method can be divided into direct test method and indirect test method [11]. Direct test method that is directly measured the thermal insulation of the sample (demagnetization of the temperature changes); indirect test method can be divided into two types:

1) Calculate the magnetic entropy change by measuring the isothermal magnetization curve;

2) By measuring the zero field and the magnetic field under the specific heat. Calculate the magnetic entropy change and the adiabatic temperature change.

2.3.1 Determination of Curie Point

Curie point is an important parameter of magnetic refrigeration material, it is necessary to carry out the determination. Common method of measuring Curie point:

1) Specific heat method (C-T curve method)

2) AC magnetic ratio method (X-T curve method)

3) DC constant field magnetization (M-T curve method)

The C-T curve is measured by the specific heat method, and then the Curie point is determined from the peak on the curve. The magnetic susceptibility method and the determination of the peak and mutation of the X-T curve determine the Curie point M-T curve method, ie, the M-T curve of the sample is measured at a constant low magnetic field (generally 200Oe. [12].

Comparison of the three methods, the best accuracy of the thermal method, and Curie point is most easy to determine. AC magnetic ratio method is slightly better than M-T curve method but due to experimental conditions and for testing convenience. Most of the M-T curve method to determine the Curie point. In general, when the M-T curve at a constant low field is measured, the Curie point is determined by the following two methods. The more formal method is: when T <Tc near the Curie point, the ferromagnetic material spontaneous magnetization strength and temperature Tc (unit K), the following rules:

M (T) = b (1-T / T0) 1/2 (2-1)

Where b is a constant and M (T) and T data are experimentally determined as M2 (T) -H / M curves [13]. The linear portion of the curve is extrapolated to M2 (T) = 0. The temperature at this time is the Curie temperature. There is also a relatively simple way is to directly M-T curve on the derivative of T, find the extreme point of the corresponding temperature that Curie point.

2.3.2 Determination of isothermal magnetization curve and calculation of magnetic entropy change

The isothermal magnetization curve is measured on a Lake shore7410 vibrating sample magnetometer.

The first step is to determine the Curie point. The M-T curves of the samples under stable external magnetic field are plotted. And the M-T curve on the derivative of T, you can get the corresponding Tc.

The second step in the Curie point near the determination of a series of isothermal magnetization curve. The magnetic entropy change is then calculated by Eq. (1-9). According to Figure 2-2 which is using numerical differentiation and integral method to simply calculate the magnetic entropy change. As follows: Discrete (1-9), the following formula can be obtained:

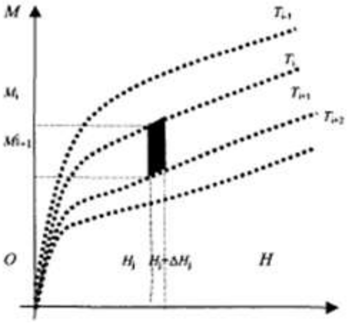


Figure 2. Schematic diagram of magnetic entropy change [14]

$$\Delta S_M\left(\left(\frac{T_i+T_{i+1}}{2}\right)\right) = \frac{1}{T_i+T_{i+1}}\sum(M_i-M_{i+1})_H \,\Delta Hj \quad (2\text{-}2)$$

Where $\Delta S_M\left(\frac{T_i+T_{i+1}}{2}\right)$ represents the magnetic entropy change of the magnetic refrigeration material at temperature $\frac{T_i+T_{i+1}}{2}$ [15]. Actually refers to the Ti, Ti + 1 temperature range of the average magnetic entropy change.

Where Mi, Mi + 1, respectively, refers to the magnetic cooling material in the magnetic field strength of Hj conditions, Ti, Ti + 1 temperature magnetization. And Δ Hj is the increase in magnetic field strength.

2.3.3 Calculate the magnetic entropy change and the adiabatic temperature change indirectly by measuring the magnetic specific heat temperature curve

The adiabatic temperature change of the magnetic entropy change can be calculated indirectly by measuring the specific heat temperature curve under the zero field and the magnetic field (Fig. 2-3). The magnetic specific heat CH-T0 curves of zero field and equal magnetic field (such as H = H0) were measured respectively. The same, in fact, the test is only a series of discrete points. The discretization of (1-11) can be changed to the following numerical integration:

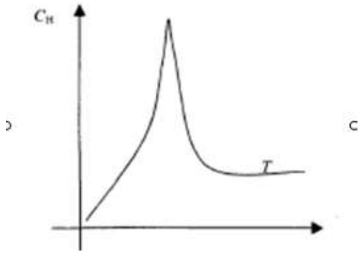


Figure 3. Determine the magnetic entropy by the curve CH-T [16]

$$S(T)\,|\,H = 0.5 \quad \sum_{i=1}^{i=N-1}\left(\frac{C_{i+1}}{T_{i+1}}+\frac{C_i}{T_i}\right)\times(T_{i+1}-T_i) \qquad (2\text{-}3)$$

(2) i.e., S (T, H = 0) and S (T, H = H0) - T curves [17] can be obtained separately for the zero field and the magnetic field.

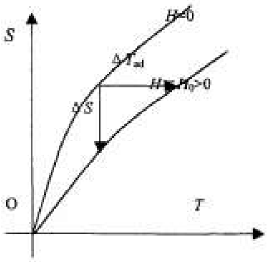


Figure 4. Schematic diagrams of isothermal magnetic entropy change and adiabatic temperature change according to magnetic specific heat [18]

According to the temperature and entropy diagram (T-S) of the zero field and the magnetic field, the magnetic entropy change SM of the magnetic field from H = 0 to H = H0 can be obtained directly at a certain isothermal temperature. It is also possible to find the adiabatic temperature change Δ Tad when the magnetic field changes from H = 0 to H = H0 under adiabatic magnetization.

3. Experimental results and analysis

3.1. Phase analysis

XRD analysis shows that this series of samples are Ho12Co7 monoclinic structure, as shown in Figure 3-1.

It can be seen from the figure that the larger the amount of Gd is, the smaller the diffraction peak angle increases as the amount of x increases,

(GdxDy1-x) 12Co7 system lattice constant and unit cell volume gradually decreased.

3.2. Curie temperature

Figure 3-2 shows the magnetization of the (GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series alloy with external temperature of 2T, which is the M-T curve.

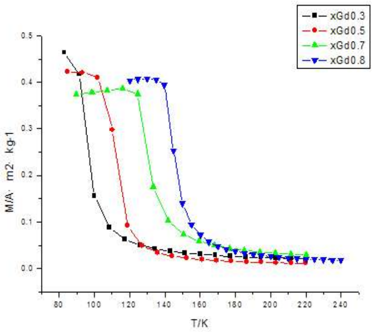


Figure 5. (GdxDy1-x) The M-T curve of the 12Co7 compound

(GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series of alloy, as shown in Figure 3-3, the temperature of the extreme curve corresponding to the temperature, that is, Curie point, as shown in Figure 3-3 Curie temperature is: (Gd0.3Dy0.7) 12Co7, Tc = 92K; (Gd0.5Dy0.5) 12Co7, Tc = 110K; (Gd0.7Dy0.3) 12Co7, Tc = 130K; (Gd0.8Dy0. 2) 12Co7, Tc = 142K. It can be seen that with the increase of Gd content, that is, x increases from 0.3 to 0.8, the Curie temperature Tc of the four alloys increases from 92K to 142K and increases linearly. The Tc-x curve is the same as the equation Tc = 100.84x + 60.76 The resulting straight line coincides, see Figure 3-4. The results were consistent with those obtained by XRD analysis.

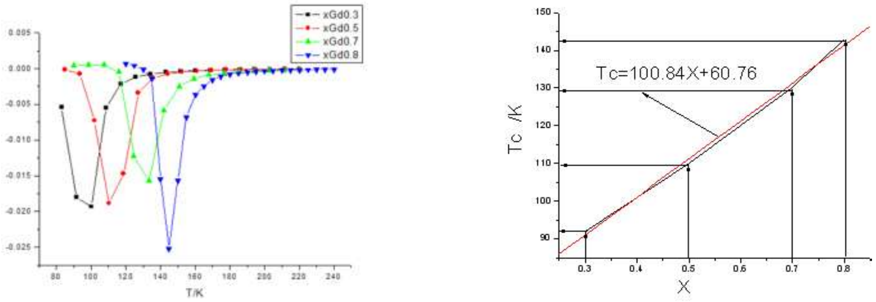


Figure 6. Derivation of the M-T curve.

When the magnetic field is 2T, the magnetic entropy change of the (GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series is shown in Fig. 3-5, and the curves are shown in Curie (Gd0.3Dy0.7) 12Co7,4.36 (J / kg · K); (Gd0.5Dy0.5) 12Co7, 6.93 (Jdb), the maximum entropy of the alloy at the Curie temperature, (J / kg · K); (Gd0.7Dy0.3) 12Co7, 4.40 (J / kg · K), (Gd0.8Dy0.2) 12Co7, 4.88 (J / kgK).

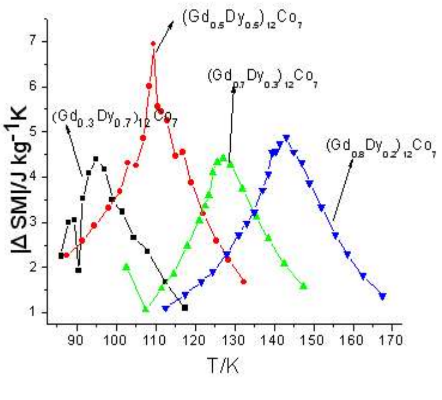


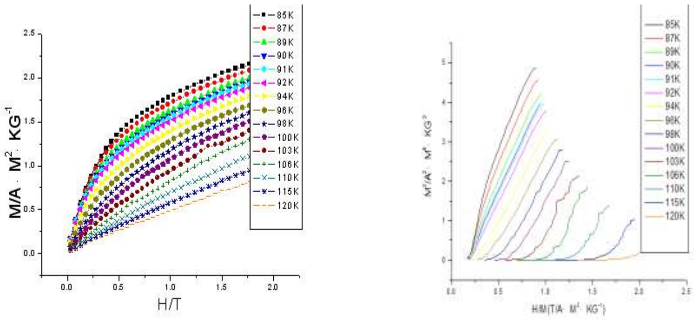
Figure 7. (GdxDy1-x) 12Co7 compound magnetic entropy change

Table 3-1 lists the maximum magnetic entropy changes of the magnetically cooled material with large Magnetocaloric effects. In contrast, (GdxDy1-x) 12Co7 has a large magnetic entropy change, especially (Gd0.5Dy0.5) 12Co7, the maximum magnetic entropy change of 7.63 J / kg · K, indicating that the magnetic properties of this material suitable for use for high temperature area of magnetic refrigeration materials.

Table 1. Representative magnetic refrigeration materials

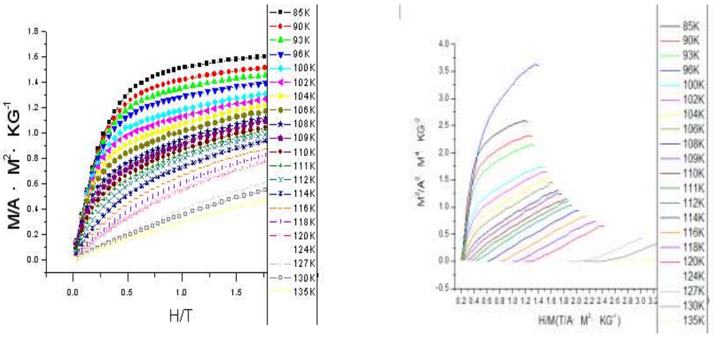
Magnetic heating material	Curie temperature Tc(K)	Plus magnetization field Variety (T)	ΔSM(J/mol·K)
TbCo2	227	1	0.9
DyCo2	140	2	7.1
La0.8Ca0.2MnO3	230	1.5	5.7
La0.802Ca0.198Mn2.99	230	1.5	5.5
La0.8Ca0.2MnO3	230	1.5	5.7
La0.802Ca0.198Mn2.99	230	1.5	5.5
Gd	293	2	5.3

Figure 3-6 to 3-9 for this experiment all the alloy material M-H map and Arrott map.



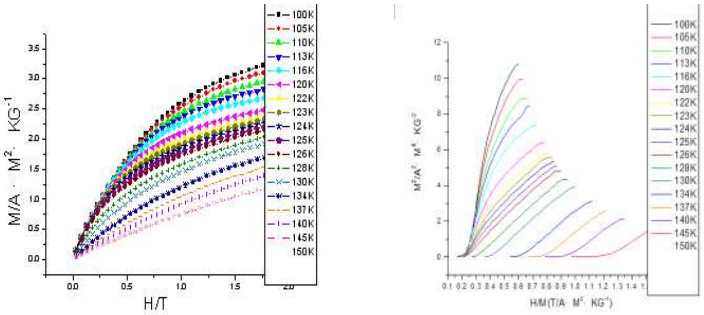
A M-T Figure b Arrott graph

Figure 8. (GdxDy1-x) 12Co7 (x = 0.3)



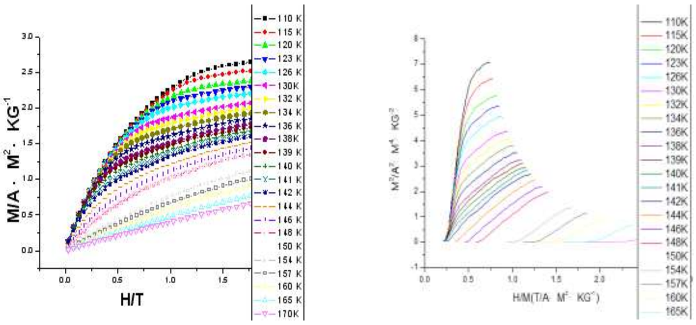
A M-T diagram Arrott map

Figure 9. (GdxDy1-x) 12Co7 (x = 0.5)



A M-T diagram Arrott map

Figure 10. (GdxDy1-x) 12Co7 (x = 0.7)



A M-T Figure b Arrott graph

Figure 11. (GdxDy1-x) 12Co7 (x = 0.8)

Through the comparison of the MT diagram of the (GdxDy1-x) 12Co7 (x = 0.3, 0.5, 0.7, 0.8) series alloy, it can be seen that the curve is near a straight line in the vicinity of Tc or Tc, Phase change, that is, when the difference between temperature and Tc is large, it is a first phase transition.

4. Conclusion

(GdxDy1-x) 12Co7 series samples are Ho12Co7 monoclinic structure, the Curie temperature Tc of the sample increases linearly with the increase of the amount of x introduced. The magnetic properties of all the samples near the Curie temperature meet the secondary phase transition law. At lower magnetic field (T = 2), the sample has a magnetocaloric effect near the Curie temperature, and the magnetic entropy becomes larger and its maximum Is 1.43 times the value of pure Gd with the magnetic field. As the Curie temperature is adjustable, the series of materials suitable for the gradient function of composite materials are expected to become a good high-temperature magnetic working fluid.

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