Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 347-353

TG(M) AND DTG(M) TECHNIQUES AND SOME OF THEIR APPLICATIONS ON MATERIAL STUDY

D. M. Lin[1], *H. S. Wang*[1], *M. L. Lin*[2], *M. H. Lin*[3] *and Y. C. Wu*[1]

[1]Department of Physics, Zhongshan University, Guangzhou 510275
[2] Analysis and Research Center, Zhongshan University, Guangzhou 510275
[3]Institute of Information and Science, Zhongshan University, Guangzhou 510275
P. R. China

Abstract

Adding a magnetic field gradient to the conventional TG system constructs the magnetic thermogravimetry analysis (TG(M) i.e. Faraday methods) and the magnetic derivative thermogravimetry (DTG(M)) techniques. We used the techniques to study the nanocrystalline processes of the FeCuNbSiB and FeCuNbCoSiB amorphous alloys. Some problems of their applications such as the characteristic temperature T_{min} and T_C are also discussed in detail.

Keywords: amorphous alloys, Fermi-Dirac distribution, nanocrystalline, phase transition and TG, TG(M) and DTG(M) techniques

Introduction

The TG(M) (Magnetic Thermogravimetric Analysis i.e. Thermomagnetometry/TM) technique is a kind of technique that we add a magnetic field gradient ($\partial H/\partial y$) on the TG system and measure the σ–T curves for the relationship between the total saturated magnetic moment per unit mass (σ) and temperature (T). The DTG(M) (Magnetic Derivative Thermogravimetry) technique can be used simultaneously to record the first derivative of the change of σ using a First Derivative Computer (FDC), i.e., to get the $d\sigma/dT$–T curve.

TM (Thermomagnetometry) is defined by the ICTA as ‘a technique in which the magnetic susceptibility of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme’. The determination of the magnetic susceptibility of a substance at various temperature has been used in inorganic chemistry for many years as a means of determining metal ion oxidation states, stereo-chemistry, Curie points, and so on. The change in the TG, or σ–T curves of substance is determined by the presence or absence of a magnetic field gradient (TG-TM). This magnetic field is supplied by either a permanent or an electromagnetic magnet. Instruments described in the literature include a helical-spring microbalance – Faraday or Gouy magnet apparatus [1–3], Ainswort semimicro recording balance – Faraday magnet apparatus [4] Perkin Elmer TGS-1 thermobalance [5] and Cahn microbalance – Faraday magnet systems [6–9]. However, in the system with the presence of a magnetic field gradient, some confusing or inaccurate concepts have been used in some papers [10, 11]. For example,

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

1. to confuse the concept of mass with magnetic force. In fact, there is substantial difference between the measured physical quality for σ–*T* and w%–*T* curve during heating, because the former has no weight (or gravity) variation caused by that of the mass of the sample during heating. In this paper, we prefer the 'σ–*T*' curve to the 'w%–*T*' curve, because there is no variation of the mass of the sample in this system during heating.

2. The minimum of the DTG curves was defined as the Curie temperature T_C' and T_C'' of Ni and $NiFe_2O_4$ salt [10], which might be not true (see the next chapter).

Recently, we have reported to use these techniques to study the process of the nanocrystallization of the FeCuNbSiB amorphous alloy [12, 13]. In this paper, we name them specially the 'TG(M)' technique and the 'DTG(M)' technique, and make further discussion of some problems on their applications in the material study, such as the characteristic temperature T_{min} (valley temperature) and T_C (Curie temperature) and the phase transition behaviour, etc.

Applications of the TG(M) and DTG(M) techniques on material study

Measuring σ and its variation rate with temperature (dσ/dT) in the magnetic materials

Figure 1 is the σ–*T* and dσ/d*T*–*T* curve of the FeCuNbSiB amorphous alloy measured by TG(M) and DTG(M) techniques during heating [13]. The variation of σ with *T* can be represented directly by the height variation Δ*h* shown on the recorder [14]. When temperature varies from the room temperature to T_C, the recorder shows the variation of height, Δ*h*=9.1 cm. According to equation (1)

$$\sigma = S\Delta h_1 \quad (1)$$

where

$$S = \sigma_o \frac{m_o}{m_1} \Delta h_o \quad (2)$$

The reciprocal of the quantity *S* is called the sensitivity of the instrument, v_o, m_o, ρ_o, are the volume, mass and density of a standard samples (such as Ni) and the saturated magnetization of which is marked as M_0 (transformed from ferromagnetism into paramagnetism). The quantity $\sigma_o = M_o/\rho_o$ is known, m_o, Δh_o and m_1 can be measured by the experiment [14].

We have calibrated the sensitivities of the instrument using standard sample, and attained that σ_o=54.69 Gs m^3 g^{-1}, m_o=2.01 mg, Δh_o=8.1 cm; and m_1=0.99 mg, Δ*h*=9.1 cm for the FeCuNbSiB amorphous alloy at room temperature, according to Eq. (1) we can get the σ_s=125 Gs cm^3 g^{-1}, this result agrees with the result reported by Müller *et al.* [15].

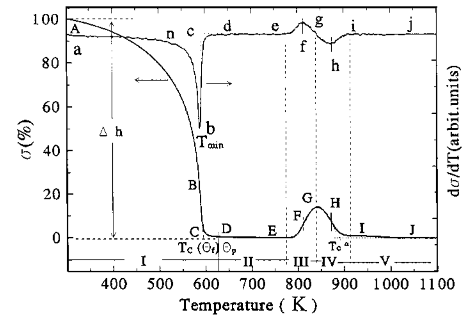

Fig. 1 σ–T and dσ/dT–T curves measured by TG(M) and DTG(M) techniques for FeCuNbSiB amorphous alloy; heating rate 10 K min^{-1}; 1 – σ–T curve of FeCuNbSiB; 2 – dσ/dT–T curves of FeCuNbSiB

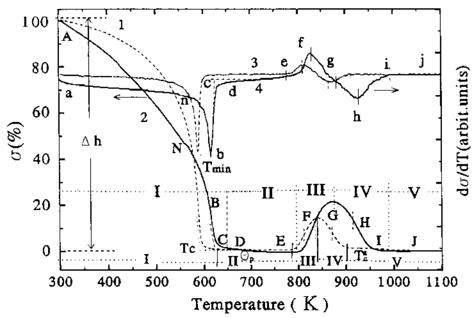

Fig. 2 σ–T and dσ/dT–T curves measured by TG(M) and DTG(M) techniques for FeCuNbSiB and FeCuNbCoSiB amorphous alloy; heating rate: 10 K min^{-1}; 1 – σ–T curve of FeCuNbSiB; 2 – σ–T curve of FeCuNbCoSiB; 3 – dσ/dT–T curves of FeCuNbSiB; 4 – dσ/dT–T curve of FeCuNbCoSi

During heating, if σ varies, the recorder will show the variation of height (Δh). The variation of σ with T can be represented directly by the height variation Δh shown on the recorder. If we normalize the σ (unity or 100%), we can get the σ–T curve, which is named the TG(M) technique. Furthermore, we can get the dσ/dT–T curve simultaneously, by means of the FDC system, which is named the DTG(M) technique (curve 2 in Fig. 1 and curves 3 and 4 in Fig. 2). The quantity of dσ/dT is the variation rate of σ with temperature in the magnetic materials.

Study on the phase transformation of magnetic alloys

The TG(M) and DTG(M) techniques are simple and very useful experimental methods for studying the phase transformation behaviour of magnetic materials. We have reported to use this technique to study the process of the nanocrystallization of the FeCuNbSiB (alloy No. 1) amorphous alloy [11]. We study further the phase transition behaviour of the FeCuNbSiB amorphous alloy with additional 4 wt% Co (alloy No. 2). Figure 2 shows the σ–T and dσ/dT–T curves of the nanocrystalline processes of the FeCuNbSiB (alloy No. 1) and FeCuNbCoSiB amorphous alloys (alloy No. 2). A small amount of Co can increase the Curie temperature of the amorphous alloy and improve the character of the nanocrystallization.

The crystallization of FeCuNbCoSiB also experiences five stages: stage I (ANBC region): the alloys are transformed from ferromagnetic amorphous phase into paramagnetic one; stage II (CDE region): the alloys are in paramagnetic amorphous state; stage III (EFG region, peak efg): the bcc α-FeSi or α-Fe (Co)Si ferromagnetic nanocrystalline phase was formed from paramagnetic amorphous state; stage IV (GHI region, valley ghi): the samples were transformed from ferromagnetic α-FeSi or α-Fe(Co)Si phase into paramagnetic one; stage V (IJ region): the samples were transformed from paramagnetic α-FeSi or α-Fe(Co)Si nanocrystalline phase into the final stable Fe_2B phases. However, there are differences of the phase transition behaviour between the FeCuNbSiB and the FeCuNbCoSiB amorphous alloys, which include the followings:

Table 1 The characteristic temperatures of the phase transition behaviour measured by TG(M) and DTG(M) techniques

Characteristic point	B	C	D	E	F	G	H	T_c^α	I
Characteristic temperature/K	T_{min}	T_c	T_p	T_E	T_F	T_G	T_H	T_c^α	T_I
Alloy No. 1	583	595	628	785	808	838	869	893	915
Alloy No. 2	610	620	650	790	828	875	921	948	985

a. Adding a small amount of Co increases evidently the characteristic temperatures of the phase transition behaviour (Table 1).

b. Adding a small amount of Co induces an obvious decrease of the σ of alloy No. 2 with temperature starting from room temperature to 573 K, but the curve of alloy No. 1 is much more precipitous than that of alloy No. 2 over 573 K. The reason might come from an increase of the ferromagnetic exchange interaction of alloy due to a small amount of Co adding.

c. Adding a small amount of Co induces a higher peak (EFGHI) of curve 2 compared to that of curve 1, and the peak efg and the valley ghi is also broaden (curves 3 and 4 in Fig. 2). It implies that alloy No. 2 can get more excellent magnetic property than alloy No. 1. Experimental result showed that when the alloys were annealed at 813 K for 1 h, we got: B_s=1.12 T, μ_{max}=20·10^4 T cm A^{-1}; for alloy No. 2 and B_s=1.05 T, μ_{max}=13·10^4 T cm A^{-1}, for alloy No. 1. A broader efg region increases a temperature range of nanocrystalline process. It is very useful for controlling the process of thermal treatment.

d. The GHI region of curve 2 is between 875 and 985 K, which increases about 30 K, compared to the region of curve 1. It shows that the transition temperature of α-Fe(Co)Si phase from ferromagnetic phase into paramagnetic one is higher than that of α-FeSi phase; i.e. T_c^α increases due to the addition of Co. Therefore, alloy No. 2 has higher thermal-magnetic stability.

Discussion on the valley temperature T_{min}, Curie temperature T_C and Θ_p of the magnetic material

Figure 1 shows the processes of transformation from ferromagnetism into paramagnetism in the FeCuNbSiB amorphous alloy. There are three characteristic temperature on the curve: T_{min}, T_C and Θ_p. Now three temperatures measured by the TG(M) and DTG(M) techniques are discussed as follows:

Physical meaning of valley temperature T_{min}

Temperature T_{min}=583 K is the minimum of the dσ/dT–T curve (the point b the minimum valley of the curve 2 in Fig. 1). It corresponds to point B at which the first derivative of σ (in the σ–T curve) with respect to T is equal to zero i.e. $(d\sigma/dT)_B=0$, and the transition rate of sample from ferromagnetic amorphous phase into paramagnetic one is the fastest at this temperature. The magnetic property is highly dependent on the energy state of metallic electrons. The energy distribution of electron in metal does not obey Boltzman's distribution but the one of Fermi-Dirac [15]. Figure 3 shows the Fermi-Dirac distribution.

According to the theory of the Pauli paramagnetism, above Fermi energy level, Fermi distribution function $\Phi(\varepsilon)\neq 0$ for $T\neq 0$, and when there is a magnetic field H, $\Phi(\varepsilon)$ is expressed in the following:

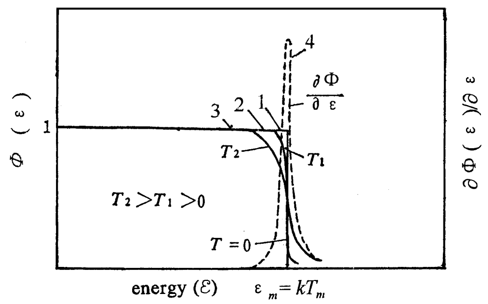

Fig. 3 Fermi-Dirac distribution; for T=0, H=0, curve 1, Fermi energy $\varepsilon=\varepsilon_f=kT_f$, $\Phi(\varepsilon)=1/[\exp(\varepsilon-\varepsilon_f)/(kT)+1]$; for $T\neq 0$, $H\neq 0$, curves 2 and 3, $\varepsilon=\varepsilon=kT_m$, $\Phi(\varepsilon)=1/[\exp(\varepsilon-\varepsilon_m)/(kT)+1]$; curve 4 is $\partial\varphi(\varepsilon)/\partial\varepsilon$ *vs.* ε, $\partial\varphi(\varepsilon)/\partial\varepsilon$ is approximately a δ function

$$\Phi(\varepsilon)=\frac{1}{\exp\left(\frac{\varepsilon-\varepsilon_m}{kT}\right)+1} \tag{3}$$

It represents the probability that these states are occupied. ε_m is Fermi energy for $T\neq 0$, and with a magnetic field H. The magnetization M is approximately expressed in the following:

$$M=H\mu_B^2\int\frac{\partial\Phi}{\partial\varepsilon}N(\varepsilon)d\varepsilon \tag{4}$$

where, μ_B is the Bohr magneton. $N(\varepsilon)$ is the density of electron distributing according to energy, and it is generally called the state density. And $\partial\Phi(\varepsilon)/\partial\varepsilon$ is approximately a δ function. Except in a very narrow range (about the width of kT), $\partial\Phi(\varepsilon)/\partial\varepsilon$ is always equal to zero, and it reaches the maximum when $\varepsilon=\varepsilon_m$, furthermore, when $T\rightarrow0$ K, $\partial\Phi(\varepsilon)/\partial\varepsilon\rightarrow\infty$. To find the derivative of $\Phi(\varepsilon)$ with respect to T, (curve 2 in Fig. 3.), we put $d\Phi(\varepsilon)/d\varepsilon=0$ and get $\varepsilon=\varepsilon_m$. Without the magnetic field, the value of ε at absolute zero is called the Fermi energy ε_f. $\varepsilon_f=kT_f$ i.e. T_f is the Fermi temperature decided by the Fermi energy ε_f ; with the presence of the magnetic field and $T\neq0$, $\varepsilon=\varepsilon_m=kT_m$, T_m has the dimension of temperature, and it tokens the necessary temperature for the electrons to transit to the energy of Fermi surface. By observing that the shapes of the curves in Figs 1 and 3 are very alike, we believe that T_m reflects the Fermi temperature decided by the Fermi energy. And the difference of T_m between the curves 3 and 4 in Fig. 2 shows that because of the increased interactive coupling due to the addition of Co, alloy No. 2 has gained obvious increase of energy which is necessary for electrons to transit to the Fermi energy and sequentially the increased thermal and magnetic stability. Therefore, the TG(M) and DTG(M) techniques may supply another way of studying the magnetic interacting influence of Co to amorphous alloy No. 1. Further study on such aspect will be reported in another paper.

Obviously T_{min} differs from the generally defined Curie temperature T_C. Some literature [10, 11] have reported to employ this instrument to measure the DTG curve of the mixtures of Ni and $NiFe_2O_4$ salt, and have taken the valley temperature T_{min} of the curve as the Curie temperature T_C of two kinds of magnetic phase. However, it might be not true.

Curie temperature T_C

Temperature T_C=595 K is the ferromagnetic Curie temperature. The characteristic point T_C is defined as the intersection of the extrapolation lines of curve ANB and the baseline EDC (i.e., the σ–T curve is extrapolated to $\sigma\rightarrow0$; Fig. 1). It reflects that the spontaneous magnetization disappears.

Curie temperature of paramagnetism Θ_p

Temperature Θ_p=628 K represents the Curie temperature of paramagnet, it is the extrapolated point on the curve of the inverse of the paramagnetic magnetic susceptibility χ with T, or it is a 'tail' appearing on the σ–T curve, (point D in Fig 1), it reflects that there should be a course for the magnetic moment to disappear. When the temperature is higher than Θ_p, the magnetic moment shows totally random statistical distribution.

Content analysis of two magnetic mixtures

Moskalewicz [10] proved that the strength of peak is related to the contents of the pure Ni and the $NiFe_2O_4$·salt existing in the sample. We used the σ–T curve of the TG(M) technique, to measure the variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a measured by DTG(M) technique (refer to Fig. 6 of paper B-35 in this issue).

Conclusions

The TG(M) and DTG(M) techniques are simple and very useful experimental methods for studying the nanocrystalline processes of the FeCuNbSiB and FeCuNbCoSiB amorphous alloys. They have wide prospect of application as a means of determining Curie points, studying the thermal interaction and magnetic interaction of alloys, etc.

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The work was supported by the Science and Technology Foundation of Guangdong Province of China.

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