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A NEW METHOD FOR STUDYING CRYSTALLIZATION OF AMORPHOUS ALLOYS

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Abstract

Experiments on the crystallization of amorphous Fe–Si–B alloys were carried out by thermogravimetric analysis (TG). This new method gives us some important information about the magnetic phase transformation of amorphous alloys, especially the magnetic volume change in crystallization beside the energy change obtained by the traditional DSC and DTA methods. Crystallization activation energies of Fe–Si–B amorphous alloy are calculated from both TG and DTA curves. The experiment also showed that the addition of Nb, Cu and Mo would influence the crystallization transition temperature of amorphous Fe–Si–B alloys greatly.

Keywords: amorphous alloy, crystallization, thermogravimetric analysis (TG)

Introduction

The nano-crystalline materials with many special and super magnetic properties could be synthesized by fractional crystallization of amorphous alloys. Since this new method for preparation of nano-crystalline materials was introduced, the crystallization kinetics of amorphous alloys has attracted more and more intensive investigations [1–3]. So far, almost all experiments on the crystallization kinetics are conducted by differential scanning calorimeter (DSC) or differential thermal analysis (DTA), which studies the transformation process by means of measuring the energy changes as function of time or temperature. However, since the micro behavior is different at the different crystallization stages of an amorphous alloy, the rate of energy change might not be proportional to its rate of volume change, so that, strictly, it is impossible, by means of a traditional thermal analysis method, to have a clear knowledge of the kinetics of the phase transformation volume. Neither can it be done by means of X-ray analysis or TEM, because much statistical work have to be done. In the

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present paper, a new thermogravimetric analysis (TG) or differential TG (DTG) method is introduced, which is very helpful in solving this important problem.

TG principle

It has been proven that TG is useful in determining the magnetic transition temperature of the Curie Temperature (T_c) of magnetic materials [4]. Its principle is as follows. Since a magnetic material is magnetic below T_c, an additional weight (an apparent weight rise) can be observed with the help of the magnetic field of the thermogravimetric analyser's furnace. If the temperature rises over T_c, there will be an apparent weight drop due to the disappearance of its magnetism. Thus the magnetic transition temperature T_c could be determined from a TG curve of weight as function of temperature.

Instead of measuring an apparent weight loss, crystallization is studied by measuring an apparent weight gain. For the crystallization process of a nonmagnetic material, since the phase which is crystallized from a nonmagnetic phase is magnetic, it will interact with the magnetic field so that we could observe an apparent weight gain. And this apparent weight increases with increasing magnetic volume and reaches a maximum at total crystallization. On this principle, we could obtain much information on crystallization by means of TG.

Experimental

Our experiments were carried out on a thermogravimetric analyzer with a high-temperature furnace (TGA7) and differential thermal analysis (DTA1700) of Perkin-Elmer Company. The Ar gas flowing through the sample chamber is 40 ml/min and a heating rate could be selected up to 100 deg·min^{-1}. The temperature error is about ±2°C for both methods. The sample of amorphous Fe–Si–B alloy foil, about 10 mm in width, 10 μm in thickness and 120~150 mg in weight, rolled as a cylinder of Φ 3 mm in diameter, and put into an Al_2O_3 cup in the sample chamber of TGA7.

Results and discussion

Determination of T_a

Since T_c represents the temperature of demagnetization usually there is only one T_c for a magnetic material. However, we observed a very interesting phenomenon that in amorphous Fe–Si–B alloys there are two T_c coupled with a magnetizing temperature T_a in between.

Figure 1 shows that the TG curves of an amorphous Fe–Si–B sample (Curve 1) and a crystallized Fe–Si–B sample (Curve 2) which was annealed at

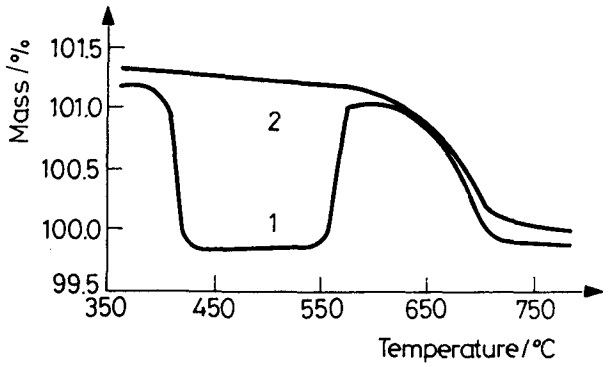

Fig. 1 Comparison of the TG curve of an amorphous sample (1) with that of a crystallized sample (2)

500°C for 1 h before measurement. In Curve 1, there are two weight losses at about 400°C (T_{c1}) and 700 °C (T_{c2}), and a weight gain at above 500°C (T_a). According to the X-ray analysis, for the crystallization of Fe–Si–B amorphous alloy, the crystalline phases crystallizing from the non-crystalline phase are αFe and Fe_2B. Considering the magnetic properties of the noncrystalline phase and the crystalline phases, it is clearly to identify that T_{c1} and T_{c2} are refer to the magnetic transition temperatures of the noncrsytalline phase and the crystalline phase respectively. Since T_{c1} is relatively low and T_{c2} is relatively high as compared with the crystallization temperature (about 450–600°C), the noncrystalline phase can be taken as a nonmagnetic phase during transformation, but in the meantime the α-Fe and Fe_2B phases are magnetic. Therefore with the development of crystallization process, there will be an increase in the magnetic volume of crystalline phase, so that we observed an apparent weight gain in the TG curve of weight as function of temperature. In Curve 2 of Fig. 1, only the T_{c2} point is found. That is because the crystalline sample consists of the magnetic αFe and Fe_2B phases transformed from the amorphous phase during annealing at 500°C for 1 h, agreeing with the results of X-ray analysis [1, 3].

Determination of activation energies

It is well known that the crystallization of amorphous alloy is closely related to time and that T_a is influenced greatly by the heating rates of measurement. By TG method, this effect can also be shown clearly. When the heating rate changes from 5 deg·min^{-1} to 40 deg·min^{-1}, the onset temperature of restored magnetism is raised from 535 to 557°C, as shown in Table 1. Meanwhile, the T_{c1} and T_{c2} do not change at all (as shown in Table 1 and Fig. 2).

In addition, the onset temperatures of the crystallization peaks of amorphous Fe–Si–B alloy measured by DTA (listed in Table 1 and Table 2) agree with the

Table 1 Data of T_{c1}, T_{c2} and T_a measured by TG at different heating rates

°C	5 deg·min^{-1}	10 deg·min^{-1}	20 deg·min^{-1}	40 deg·min^{-1}
T_{c1}	410	412	410	410
T_{c2}	700	701	701	703
T_a	535	545	551	557

T_a refers to the onset temperature of the larger peak of DTG

corresponding values obtained by TG, only a few degrees higher. It indicates that for this stage of crystallization, the rate of the change of magnetic volume measured by TG is close to that of energy release measured by DTA. However if we compare the entire peak of crystallization of DTG with that of DTA measured by the same heating rate, there is an obvious difference between them, especially for the peak temperature and the final offset temperature. For some of them, the difference of temperature is even more than 38°C and the difference of activation energy is more than 263 kJ·mol^{-1} (as shown in Table 2 and Fig. 3). These results indicate that TG is quite different from DTA as a whole.

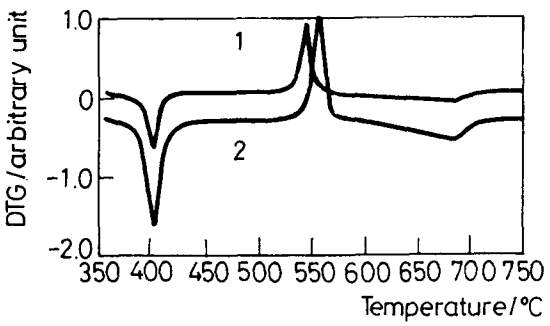

Fig. 2 Comparison of DTG curve of 10 deg·min^{-1} (1) and that of 40 deg·min^{-1} (2)

Based on the kinetic method of Doyle-Ozawa [3, 5], the apparent activation energy for the onset temperature of the large peak is calculated about 486 kJ·mol^{-1} for TG, using T_a data listed in Table 2, which are similar to those of DTA. But the activation energies of the other corresponding temperatures are quite different form the two methods. It indicates that their mechanism and behaviours are different at different crystallization stages. This is because the measuring quantities of the two methods are quite different. For TG, were obtained the apparent weight change which refers to the magnetic volume change during crystallization, whereas for DTA, we measured the energy change during transformation. Therefore, although both TG and DTA could be used to study the crystallization of amorphous alloys, their results are quite different. Furthermore, this difference is very important, in some sense, it would give us a deep understanding of the crystallization process of amorphous Fe–Si–B alloys.

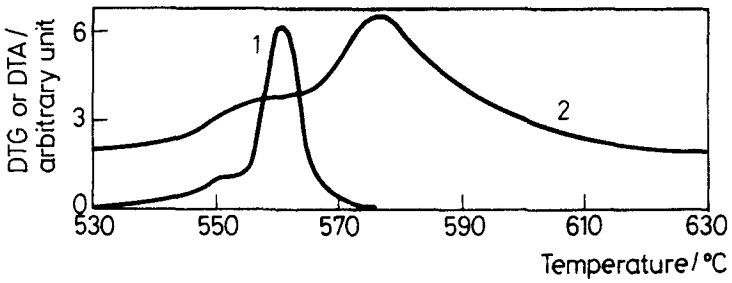

Fig. 3 Comparison of TG curve (1) and DTA curve (2) at 40 deg·min^{-1}

Table 2 The corresponding temperatures of DTG and DTA curves at different heating rates

		5 deg·min^{-1}	10 deg·min^{-1}	20 deg·min^{-1}	40 deg·min^{-1}	E_c /kJ·mol^{-1}
Onset*/°C	TG	515	524	532	545	357
	DTA	521	528	539	549	374
Onset /°C	TG	535	545	551	557	486
	DTA	537	545	552	563	437
Peak/°C	TG	540	548	557	561	496
	DTA	548	554	565	577	387
Offset/°C	TG	544	555	563	566	471
	DTA	549	559	577	604	208

*Corresponding to the smaller peak

Effect of alloying element on T_a

According to the above discussion, TG could be used to study the crystallization of the amorphous alloy systems in which the crystallization transition temperature (T_a) is higher than the Curie Temperature of the noncrystalline phase but lower than that of the crystallized phases.

Considering the magnetic properties of these crystalline phases, in addition to amorphous Fe–Si–B alloy system, TG is also suitable to study other amorphous alloy systems such as Fe–Nb–Si–B, Fe–Cu–Si–B, Fe–Cu–Nb–Si–B, Fe–Cu–Mo–Si–B, Ni –P, Co–B, Co–Cu –B, Co–Ni–B, Co–Zr. Here are some experiments on the influence of other alloying elements on the crystallization transition temperature of Fe–Si–B alloy system. For the Fe–Si–B amorphous samples with 1% Nb, 1% Cu and 3% Nb, 1%Cu and 1%Mo, the T_a temperatures are respectively 602, 539 and 514°C, determined from the TG curves of

40 deg·min^{-1}. These results clearly show that the addition of Nb, Cu and Mo could changed the crystallization transition temperature greatly, agreeing with the results obtained by DTA and DSC [3].

Conclusion

TG is a good experimental method which is suitable to study of the crystallization of Fe–Si–B and other amorphous alloys. And it is quite different from the traditional DTA and DSC methods. We could get direct information on the magnetic volume change during transformation from this new method.

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Zusammenfassung — Mittels TG wurden Versuche zur Kristallisation von amorphen Fe–Si–B-Legierungen durchgeführt. Diese neue Methode liefert einige wichtige Informationen über die magnetische Phasenumwandlung amorpher Legierungen, insbesondere die magnetische Volumenänderung bei der Kristallisation sowie der Energieänderung aus herkömmlichen DSC- und DTA-Methoden. Die Aktivierungsenergie für die Kristallisation von amorphen Fe–Si–B-Legierungen wurde sowohl anhand der TG- als auch der DTA-Kurven berechnet. Das Experiment zeigte weiterhin, daß der Zusatz von Nb, Cu und Mo die Kristallisations-Umwandlungstemperatur amorpher Fe–Si–B-Legierungen beträchtlich beeinflußt.