Critical Cooling Rate for the Glass Formation of Ferromagnetic $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ Alloy

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In this paper the critical cooling rate, R_c , for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy has been determined using both Uhlmann's and Barandiaran-Colmenero's method. In Uhlmann's method, all kinds of the expressions of $\Delta G^{l-s}(T)$ and $\eta(T)$ determined using the different modes and methods had been investigated. It is indicated that the R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy can be estimated to be 349 K/s by Uhlmann's method based on the appropriate expressions of $\Delta G^{l-s}(T)$ and $\eta(T)$. The calculated result accords with our experimental result. The R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy has also been determined to be 0.49 K/s using Barandiaran-Colmenero's method. This resultant R_c is unreasonable low and it indicates that Barandiaran-Colmenero's method does not suit to Fe-based alloy.

KEY WORDS: Glass formation ability; Critical cooling rate; $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy

1. Introduction

$\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy is the first magnetic amorphous alloy and was first synthesized by Duwez and Lin^[1]. This alloy has excellent soft magnetic properties and had been extensively studied for the subsequently several decades. The critical cooling rate, R_c , for the glass formation of this alloy had been estimated in many references and until now the lowest one was $\sim 1.8 \times 10^4$ K/s^[2]. It was generally believed that this alloy cannot be prepared in a bulk amorphous form due to low glass forming ability. However, more recently, the bulk magnetic $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ glassy alloy rods with a maximum diameter of ~ 2.0 mm was prepared by the combination method of fluxing technique and J-quenching technique^[3]. The corresponding R_c for the glass formation of this alloy is estimated to be below 10^3 K/s^[4]. Thus it is necessary to re-estimate the R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy.

R_c is the lowest cooling rate for solidifying the liquid of a glass-forming material without crystallization. A number of methods have been devised to determine R_c . The most common method is to construct

time-temperature-transformation (TTT) curve for the evaluation of R_c based on homogeneous nucleation mechanism developed by Uhlmann^[5]. Improvement for this method to get a more realistic estimate of R_c is to construct continuous-cooling-transformation (CCT) curve instead of TTT curve. This type of calculation has been successfully applied to many glass-forming systems^[6,7]. However in order to implement Uhlmann's method, the temperature dependences of many thermal parameters in the undercooled region of alloy, such as the difference of molar Gibbs free energy between liquid and solid ΔG^{l-s} , viscosity η and so on, are required. But the metastable nature of the undercooled phase makes it difficult to obtain these thermal parameters of the alloy experimentally. Only for Zr-based and Pd-based alloys which have a relative large stability in the undercooled region, the numerous thermodynamic data had been obtained experimentally. As a result, the R_c for the glass formation of Zr-based and Pd-based alloys can be calculated by Uhlmann's method and the resultant results well accord with actual situation. But for Fe-based alloy, due to lack of data for thermal parameters in the undercooled region, it is difficult to obtain reliable R_c for the glass formation by Uhlmann's method.

Besides Uhlmann's method, the R_c for the glass formation can also be experimentally estimated from

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measurements on cooling rate dependence of the offset temperature for fusion and the onset temperature of solidification using differential thermal analysis (DTA) developed by Barandiaran and Colmenero^[8]. Compared with Uhlmann's method, Barandiaran-Colmenero's method is simple, and none predetermined parameters are required. However the validity of this method for Fe-based amorphous alloys needs to be verified.

In this paper, the determination of R_c for the glass formation for Fe₈₀P₁₃C₇ alloy by both Uhlmann's and Barandiaran-Colmenero's methods is presented. Because of lacking experimental data, some theoretical models have to be employed during calculation in order to give the temperature dependences of the required thermal parameters in the undercooled region of Fe₈₀P₁₃C₇ alloy, and all kinds of theoretical models of difference of Gibbs free energy between liquid and solid $\Delta G^{l-s}(T)$ and viscosity $\eta(T)$ in the undercooled region of Fe₈₀P₁₃C₇ alloy have been examined also. The main purpose of this work is to reveal which methods and theoretical models are suitable to be employed for determining R_c for the glass formation of Fe-based alloy by checking whether the obtained results are rational.

2. Calculation Methods for R_c for the Glass Formation of Fe₈₀P₁₃C₇ Alloy

2.1 Uhlmann's method

Along with Uhlmann's method, the TTT curve of the alloy can be constructed based on homogenous nucleation mechanism.

When the volume fraction of the crystallized material X in an undercooled liquid alloy is small, X can usually be described very well by the Johnson-Mehl-Avrami equation:

$$X = \frac{\pi}{3} I_s U^3 t^4 \quad (1)$$

where I_s is the steady-state nucleation frequency, U is the crystal growth velocity, and t is the time taken for X to appear.

The I_s can be written as^[9]

$$I_s = \frac{8n^{*2/3} N_A k_B T}{\eta(T) a_0^3 V_m} Z \exp\left(-\frac{\Delta G_n^*}{k_B T}\right) \quad (2)$$

where $\eta(T)$ is the viscosity of molten alloy, a_0 is the atomic jump distance, V_m is the molar volume, k_B is the Boltzman constant, T is the temperature, and N_A is the Avogadro's number. To evaluate some of these parameters, the density of the bulk amorphous Fe₈₀P₁₃C₇ alloy has been measured by means of immersed water method at room temperature. It is equal to $7.51 \times 10^3 \text{ kg/m}^3$. For simplicity, the temperature dependence of the density is ignored. And the molar mass of Fe₈₀P₁₃C₇ alloy is $49.55 \times 10^{-3} \text{ kg/mol}$. Thus it can be deduced that $V_m = 6.60 \times 10^{-6} \text{ m}^3$ and

$a_0 = 0.223 \text{ nm}$. The factor Z is called the Zeldovich factor and in most cases, $0.01 < Z < 0.1$. Here $Z = 0.05$ is chosen.

n^* is the critical cluster size and is given by

$$n^* = \frac{32 N_A \pi}{3 V_m} \frac{\sigma^3}{|\Delta G_V^3|} \quad (3)$$

where ΔG_V is the Gibbs free energy difference from the liquid phase and the solid phase per unit volume and can be expressed as $\frac{\Delta G^{l-s}}{V_m}$ where ΔG^{l-s} is the molar Gibbs free energy difference from the liquid phase and the solid phase, σ is the interface energy between the solid phase and liquid phase per unit area.

ΔG_{n^*} is the nucleation barrier for the formation of the critical nucleus and is given by

$$\Delta G_{n^*} = \frac{16\pi}{3} \frac{\sigma^3}{\Delta G_V^2} \quad (4)$$

The crystal growth velocity U can be expressed by^[10]

$$U = \frac{f k_B T}{3 \eta(T) a_0^3} \left[1 - \exp\left(-\frac{\Delta G^{l-s}}{k_B T}\right) \right] \quad (5)$$

where f is the fraction of sites on the interface where atoms may preferentially be added and removed. For metallic materials, f can be expressed as $f = 0.2 \Delta T_r^{[5]}$, where ΔT_r is the reduced undercooling and defined as $\frac{T_m - T}{T_m}$ where T_m is the melting temperature.

The overall transformation kinetics of the amorphous alloy can be constructed if all parameters in the above equations such as ΔG^{l-s} , σ , $\eta(T)$ and so on can be determined.

2.1.1 Estimation of the difference of Gibbs free energy between solid and liquid

The Gibbs free energy difference between the liquid and crystalline phases is given by

$$\Delta G^{l-s} = \Delta H^{l-s} - T \Delta S^{l-s} \quad (6)$$

where

$$\Delta H^{l-s} = \Delta H_m - \int_T^{T_m} \Delta C_P^{l-s} dT \quad (7)$$

$$\Delta S^{l-s} = \Delta S_m - \int_T^{T_m} \frac{\Delta C_P^{l-s}}{T} dT \quad (8)$$

where ΔS_m and ΔH_m are the molar entropy and the enthalpy of fusion of the alloy and they are related to each other by the equation of $\Delta H_m = T_m \Delta S_m$. ΔC_P^{l-s} is the difference in specific heats of liquid phase and crystalline phase. In the case of the non-availability of ΔC_P^{l-s} , some approximated theoretical models have been proposed and results in the different expressions for ΔG^{l-s} .

At first ΔC_P^{l-s} is frequently assumed to be a constant under condition of a small undercooling. So ΔG^{l-s} can be written as

$$\Delta G^{l-s} = \frac{\Delta H_m(T_m - T)}{T_m} + \Delta C_P^{l-s} \left(T \ln \frac{T_m}{T} - T_m + T \right) \quad (9)$$

Hoffman^[11] had chosen the temperature T_α at which $\Delta H^{l-s}=0$. Assuming $T_\alpha \ll T_m$, Eq. (9) can be simplified as

$$\Delta G^{l-s} = \Delta H_m \frac{(T_m - T)T}{T_m^2} \quad (10)$$

Thompson and Spaepen^[12] had chosen the temperature T_0 at which $\Delta S^{l-s}=0$ and thus gave $\Delta C_P^{l-s} = \frac{\Delta H_m}{T_m}$. For further simplification, the following approximation was used:

$$\ln \frac{T_m}{T} \approx \frac{2(T_m - T)}{T_m + T} \quad (11)$$

Substituting $\Delta C_P^{l-s} = \frac{\Delta H_m}{T_m}$ and the above equation into Eq. (9), ΔG^{l-s} can be expressed as

$$\Delta G^{l-s} = \frac{\Delta H_m \times 2 \times (T_m - T)T}{T_m(T_m + T)} \quad (12)$$

Along the method of Thompson and Spaepen's, Lad *et al.*^[13] use more strictly approximation as the following:

$$\ln \frac{T_m}{T} \approx 2 \times \left[\frac{T_m - T}{T_m + T} + \frac{1}{3} \left(\frac{T_m - T}{T_m + T} \right)^3 \right]$$

Substituting the above equation into Eq. (9), ΔG^{l-s} can be written as

$$\Delta G^{l-s} = \frac{\Delta H_m \times 2 \times (T_m - T)T}{T_m(T_m + T)} \left[1 + \frac{(T_m - T)^2}{3(T_m + T)^2} \right] \quad (13)$$

Besides assuming ΔC_P^{l-s} to be a constant, Ji and Pan^[14] proposed $\Delta C_P^{l-s} = \frac{\Delta H_m}{T}$ based on the experimental data of ΔC_P^{l-s} of $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ alloy. So ΔG^{l-s} can be expressed as

$$\Delta G^{l-s} = \frac{2 \times \Delta H_m(T_m - T)}{T_m} \left[\frac{T}{T + T_m} - \frac{T_m(T_m - T)^2}{3(T_m + T)^3} \right] \quad (14)$$

ΔH_m of $Fe_{80}P_{13}C_7$ alloy is 10.6 kJ/mol determined from DTA curve. So the function curves of $\Delta G^{l-s}(T)$ for $Fe_{80}P_{13}C_7$ alloy obtained using from Eq. (10) to Eq. (13) are shown in Fig.1.

2.1.2 Estimation of the interfacial free energy of the solid/liquid interface

The interfacial free energy of the solid/liquid interface, σ , according to the broken-bond model, can be written as^[15]

$$\sigma = \alpha \frac{\Delta H_m}{(N_A V_m^2)^{1/3}} \quad (15)$$

where α is the packing factor for the given structure. For the glass formation alloys the nucleation barrier

Fig. 1 The relationship between T and ΔG^{l-s} for $Fe_{80}P_{13}C_7$ alloy determined by the different expressions

ΔG_n^* is about $60 k_B T$ at $\Delta T_r = 0.2$. Thus α can be assumed to have a value of 0.41.

2.1.3 Estimation of the viscosity of $Fe_{80}P_{13}C_7$ alloy

In order to construct TTT curve, the temperature dependence of the viscosity η of $Fe_{80}P_{13}C_7$ alloy will be required. However, such knowledge is not available at present and the estimation has to be carried out.

The estimation of the viscosity η of $Fe_{80}P_{13}C_7$ alloy is based on the widely accepted Vogel-Fulcher's equation:

$$\eta(T) = A \exp \left(\frac{B}{T - T_0} \right) \quad (16)$$

where A , B and T_0 are constants. A , B and T_0 need to be determined in order to obtain the expression of the viscosity η .

Chen^[16,17] and other workers^[18–20] have shown that the apparent activation energies, $E(T)$, for glass transition and crystallization in some metallic and oxide glasses coincide with those for viscous flow. This coincidence implies that both the rates of the glass transition and crystallization in metallic glass scale as that of viscosity. The apparent activation energies for viscous flow as a function of temperature are given by

$$E(T) = R \frac{d(\ln(\eta))}{d(1/T)} = \frac{RBT^2}{(T - T_0)^2} \quad (17)$$

So the apparent activation energies for the glass transition (E_g) and crystallization (E_p) can be obtained by using the Kissinger plot^[21]:

$$\ln \left(\frac{T_g^2}{\phi} \right) = \frac{E_p}{RT_g} + \text{constant} \quad (18)$$

where T_g is the transition temperature as a function of the heating rate ϕ in the thermal analysis. Fig. 2 shows the Kissinger plots for glass transition and crystallization of bulk $Fe_{80}P_{13}C_7$ amorphous alloy specimens. The apparent activation energies for glass transition E_g and E_p can be determined to be 857 and 488 kJ/mol, respectively. In addition the glass transition temperature T_g and the crystallization temperature T_p can be determined to be 675 and 710 K from DSC curve at the heating rate of 0.33 K/s, respectively.

Fig. 2 DSC curves of as-prepared bulk Fe₈₀P₁₃C₇ amorphous alloys with different heating rates (ϕ) (a) and the Kissinger plots for the glass transition (T_g) and crystallization (T_p) of bulk Fe₈₀P₁₃C₇ amorphous alloy (b)

Here some different methods were used to determine A , B and T_0 in Eq. (16) so as to establish the temperature dependence of the viscosity of Fe₈₀P₁₃C₇ alloy in the undercooled liquid region. These methods arose from the different choices of η or $E(T)$ at the different temperatures used.

2.1.3.1 Method (a)

By taking $\eta(T_m)=5$ Pa·s and $\eta(T_g)=10^{12}$ Pa·s for Fe₈₀P₁₃C₇ alloy together with the equation of $E_g = \frac{RBT_g^2}{(T_g-T_0)^2}$, the expression of $\eta(T)$ can be given by

$$\eta(T) = 7.3 \times 10^{-3} \exp\left(\frac{4681}{T - 531}\right) \quad (19)$$

2.1.3.2 Method (b)

By taking $\eta(T_m)=5$ Pa·s and $\eta(T_g)=10^{12}$ Pa·s for Fe₈₀P₁₃C₇ alloy together with the equation of $E_p = \frac{RBT_p^2}{(T_p-T_0)^2}$, the expression of $\eta(T)$ can be obtained as

$$\eta(T) = 6.0 \times 10^{-1} \exp\left(\frac{5313}{T - 486}\right) \quad (20)$$

2.1.3.3 Method (c)

By taking $\eta(T_g)=10^{12}$ Pa·s for Fe₈₀P₁₃C₇ alloy together with the equations of $E_p = \frac{RBT_p^2}{(T_p-T_0)^2}$ and $E_g = \frac{RBT_g^2}{(T_g-T_0)^2}$, the expression of $\eta(T)$ can be written as

$$\eta(T) = 3.3 \times 10^5 \exp\left(\frac{704}{T - 619}\right) \quad (21)$$

2.1.3.4 Method (d)

By taking $\eta(T_m)=5$ Pa·s for Fe₈₀P₁₃C₇ alloy together with the equations of $E_p = \frac{RBT_p^2}{(T_p-T_0)^2}$ and $E_g = \frac{RBT_g^2}{(T_g-T_0)^2}$, the expression of $\eta(T)$ can be written as

$$\eta(T) = 3.3 \times 10^{-1} \exp\left(\frac{1819}{T - 585}\right) \quad (22)$$

However, with Eq. (20) obtained by method (c), $\eta(T_m)$ of the specimen will be given an unsubsistent

large viscosity of 1.0×10^7 Pa·s. Likewise, with Eq. (21) obtained by method (d), $\eta(T_m)$ of the specimen will be given an unsubsistent low viscosity of 2.0×10^8 Pa·s. It is indicated that Eqs. (20) and (21) are not the plausible expression of the viscosity of the specimen. Only the expressions of $\eta(T)$ determined by method (a) and (b) were considered in the following discussion.

2.1.4 Determination of R_c from TTT and CCT Curves

Based on the above efforts, a TTT diagram corresponding to a volume fraction of $X=10^{-6}$, which is considered to be a just detectable concentration of crystals^[5], can now be constructed. By substituting the different expressions of $\eta(T)$ obtained by using methods (a) and (b) and the different expressions of ΔG^{l-s} from Eq. (10) to Eq. (13), the corresponding TTT curves for Fe₈₀P₁₃C₇ alloy were obtained. So the R_c for the glass formation of Fe₈₀P₁₃C₇ alloy can be given by

$$R_c \approx \frac{T_m - T_n}{t_n} \quad (23)$$

where T_m is the melting temperature, T_n and t_n are the temperature and time corresponding to the nose of TTT curve, respectively. A more realistic estimate of R_c can be obtained from CCT curve instead of TTT curve. Based on the Scheil additivity rule^[22], CCT curves can be constructed from the corresponding TTT curves. Fig. 3 shows a few typical TTT (solid lines) and the corresponding CCT (dashed lines) curves of Fe₈₀P₁₃C₇ alloy. As shown in Fig. 3, the R_c position of the nose of CCT curve moves down and back relative to that of the corresponding TTT curve. Thus the R_c determined from CCT curves using Eq. (22) are lower than those determined from TTT curves. The critical cooling rates are summarized in Table 1. From Table 1 it can be found that the R_c from CCT curves are about 1/3 of that from TTT curves for all kinds of cases.

Fig. 3 TTT and CCT curves constructed by using the different Gibbs free energy obtained from Eq. (10) (a), Eq. (11) (b), Eq. (12) (c) and Eq. (13) (d) with the viscosity determined by method (a)

Table 1 The critical cooling rates R_c (K/s) for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy determined from TTT and CCT curves which are constructed with the ΔG^{l-s} that calculated by Eqs. (10), (12), (13) and (14) and the $\eta(T)$ determined by method (a) and (b)

Corresponding curve		R_c (K/s) constructed with the different expressions of ΔG^{l-s}			
		Eq.(10)	Eq.(12)	Eq.(13)	Eq.(14)
TTT	$\eta(T)$ determined by	1.2×10^4	1.1×10^3	2.3×10^3	3.1×10^3
CCT	method (a)	3.7×10^3	349	730	1.2×10^3
TTT	$\eta(T)$ determined by	2.4×10^4	3.1×10^3	2.8×10^3	5.4×10^3
CCT	method (b)	7.7×10^3	1.0×10^3	798	1.8×10^3

2.2 Barandiaran-Colmenero's method

By considering the liquid-solid transformation behaviour under non-isothermal conditions, Barandiaran and Colmenero^[8] have obtained a relation which enables the critical cooling rate, R_c , to be evaluated from thermal analytical measurements. The relation is

$$\ln R_r = \ln R_c - \frac{C}{(T_L - T_{XC})^2} \quad (24)$$

where R_r is the cooling rate, T_L is the offset temperature of fusion, and T_{XC} is the onset temperature of solidification and C is a constant. By measuring T_L upon melting at a constant heating rate and T_{XC} upon cooling at different cooling rates R_r using thermal analytical techniques, the R_c for the glass formation can be determined from the plot of $\ln R_r$ against $1/(T_L - T_{XC})^2$.

3. Results and Discussion

Most recently, bulk magnetic $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ glassy

alloy rods with a maximum diameter of 2.0 mm had been prepared by fluxing technique and novel J-quenching technique^[3]. The cooling rate of the specimen with the diameter of 2.0 mm in J-quenching technique can be estimated to be below 10^3 K/s^[4]. The R_c for the glass formation of an alloy should be determined based on homogenous nucleation mechanism. However heterogeneous impurities cannot be avoided entirely under the laboratory conditions. So the R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy should be adequately lower than 10^3 K/s. Based on the above estimation, it can be decided which the calculated R_c in Table 1 are reasonable and which the expressions of and obtained using the different methods are appropriate for $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy.

3.1 Uhlmann's method

3.1.1 Effect of the difference of Gibbs free energy between solid and liquid

At first these resultant R_c determined by CCT

curves using the different expressions of $\eta(T)$ obtained by method (a) in Table 1 are investigated. It indicates that R_c obtained using the difference expressions from Eq. (10) to Eq. (13) can vary within two orders of magnitude. And only the results for Eq. (11) and (12) are placed in the reasonable range. Comparatively, the result obtained by Eqs. (11) is more suitable for Fe₈₀P₁₃C₇ alloy than that with Eq. (12). Similar results have also been found in those cases as using $\eta(T)$ obtained by method (b).

In fact all equations from Eqs. (10) to (13) are approximated expressions of Eqs. (9), (11) and (12) are obtained from the same hypothesis, therefore, which should appropriate for determining ΔG^{l-s} for Fe-based alloys. Eq. (13) is proposed based on the experimental data of Zr₅₇Cu_{15.4}Ni_{12.6}Al₁₀Nb₅ alloy and seems not to be suitable for Fe-based alloys. Cai *et al.*^[23] proposed that the expressions of ΔG^{l-s} of the amorphous alloys can be reasonably chosen based on the reduced glass transition temperature $T_{rg} = T_g/T_L$, which is the most common empirical criterion for quantifying glass forming ability (GFA) of amorphous alloys. They considered all kinds of the expressions of ΔG^{l-s} and proposed that Eq. (11) and (12) are suitable for amorphous alloys with the smallest T_{rg} . Compare with other amorphous alloys, Fe-based amorphous alloys have lower GFA and smaller T_{rg} .

3.1.2 Effect of the viscosity

Compare with the resultant R_c determined by CCT curves using $\eta(T)$ obtained by method (a) and (b) in Table 1, these results are not largely deviate from each other for the different expressions of ΔG^{l-s} and the R_c with $\eta(T)$ determined by method (a) are lower than that with $\eta(T)$ determined by method (b). Comparatively, method (a) gives a more realistic estimate for $\eta(T)$ of Fe₈₀P₁₃C₇ alloy than method (b).

In fact the choice of the expression of $\eta(T)$ is crucial for the calculation of R_c in Uhlmann's method. However, due to the lack of both the experimental data and the theoretical models about the dependence of viscosity on temperature of metallic glasses, especially Fe-base metallic glasses, not too much attempts to determine the dependence of viscosity on temperature had been investigated in this paper. In addition, it is assumed that the dependence of viscosity of the alloy on temperature accords with Vogel-Fulcher's expression in both method (a) and method (b). However it had been pointed out in many studies^[24,25] that a Vogel-Fulcher's expression with one set of constants may be unsuitable for a metallic glass to fit the whole range of viscosities from the T_g to T_m . In a word, further progress on the viscosity of metallic glasses is needed in order to exactly estimate the R_c for the glass formation of metallic glasses, especially Fe-based metallic glasses.

3.2 Barandiaran-Colmenero' method

The DTA curves of the Fe₈₀P₁₃C₇ bulk amorphous

alloy at the cooling rates of 0.083, 0.17, 0.33 and 0.50 K/s are shown in Fig. 4(a). The plot of $\ln R_c$ vs. $1/(T_L - T_{XC})^2$ obtained using the data deduced from the DTA measurements is shown in Fig. 4(b). Thus the R_c for the glass formation of the Fe₈₀P₁₃C₇ alloy is determined to be 0.49 K/s based on Eq. (23). The resultant R_c is shockingly low. Until now few works about the calculation of R_c for Fe-based alloys using Barandiaran-Colmenero' method have been reported. Based on Barandiaran-Colmenero's method, the R_c of Fe₆₁Co₅Zr₈Y₂Cr₂Mo₇B₁₅^[26], Fe₄₈Cr₁₅Mo₁₄C₁₅B₆Y₂ and Fe₄₁Co₇Cr₁₅Mo₁₄C₁₅B₆Y₂^[27] alloys are determined to be 37, 11.2 and 6.5 K/s, respectively. It is indicated that the resultant R_c for Fe-based alloys using Barandiaran-Colmenero' method are all quite low. However, it is reported that the R_c for the glass formation for Zr-based determined using Barandiaran-Colmenero's method are in the orders of 10 K/s^[28,29]. It is well known that the glass-forming ability (GFA) of Zr-based alloy is much larger than that of Fe-based alloy. So it seems that Barandiaran-Colmenero's method is not suitable for determination of the R_c for the glass formation for Fe-based alloy. The R_c for Fe-based alloys are very large and only the dozens of cooling rates using in the measurement of DTA cannot reflect the crystallization kinetic behavior of Fe-based alloy under the large undercooling well. This may lead to the failure of Barandiaran-Colmenero's method to determine the R_c for the glass formation for these alloys with a low GFA just like Fe-based alloy.

Fig. 4 DTA cooling curves of Fe₈₀P₁₃C₇ alloy at various cooling rates (R_r) (a) and the critical cooling rate plot of $\ln R_c$ vs. $1/(T_L - T_{XC})^2$ (b)

4. Conclusions

The R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy has been estimated using both Uhlmann's method and Barandiaran-Colmenero's method. In Uhlmann's method, all kinds of the expressions of ΔG^{l-s} and $\eta(T)$ determined using the different modes and methods had been investigated. It is indicated that Eq. (12) for ΔG^{l-s} and methods (a) for $\eta(T)$ give the best estimation for the R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy and the resultant R_c is 349 K/s determined from CCT curve. The calculated result accords with our experimental result^[3] and meantime it is indicated that the heterophase impurities have been controlled well in J-quenching technique. In addition, the R_c for the glass formation of $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ alloy has also been determined to be 0.49 K/s based on Barandiaran-Colmenero's method. But this resultant R_c is unreasonable low and it shows that Barandiaran-Colmenero's method is not suit to Fe-based alloy.

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