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Calculating activation energy of amorphous phase with the Lambert W function

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Abstract A new approach for determining the activation energy of amorphous alloys is developed. Setting the second order differential coefficient of heterogeneous reaction rate equation of non-isothermal heating as zero at extreme points of DSC curve, we obtain the new correlation taking form:

$$\gamma_1 = Lambertw(\gamma_3 e^{-\gamma_2}) + \gamma_2$$

where γ_1, γ_2 and γ_3 are symbols comprising parameters, and *Lambertw*(…) is the Lambert W function symbol. Through this function, the activation energy can be calculated with DSC test at single heating rate without the isoconversion assumption. To evaluate the feasibility of calculating the activation energy with the new method, the glass transition activation energy of as-cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy is measured. The value is 1.6 eV, which agrees well with the result of viscosity measurements. Thus, it is a good possibility that the new approach can be used to determine the activation energy of amorphous phase.

Keywords Activation energy · Bulk amorphous alloys · Lambert W function · Structure relaxation

Introduction

The structure relaxation of materials is caused by variation of the structure defects concentration [1, 2]. Atoms transport and rearrangement in that course, which need an amount of activation energy to span the thermodynamic potential barriers that influences the structure relaxation kinetics significantly. Thus, evaluating the activation energy is important work to study structure relaxation, which has led to a series of calculating methods over the past decades. The main methods include the Freeman–Carroll and Ellerstein methods [3], the Achar–Brindley–Sharp method [4], the Chatterjee method [5], the temperature criterion method [6], the non-parametric kinetics method [7, 8] and the isoconversion methods [9–19]. Generally, the fore five out of seven methods have been proven to be unreliable, especially for complicated solid-state reactions [20–23], the last out of seven methods may be the most popular way for detecting effective activation energy [24]. Isoconversional methods require the determination of the temperatures at which an equivalent stage of the reaction for various heating rates.

They can be classified into two types. Type A includes differential methods that make no mathematical approximations. Type B methods make use of various approximations of the temperature integral so that their accuracy is dependent on the accuracy of the approximation [17, 24, 25].

In previous studies, Isoconversion methods have been used widely to determine the activation energies of amorphous phases, especially for metallic glasses [26–28]. However, there is no a priori reason to believe that these methods are also applicable to the glass transition in metallic glasses [29]. To clear that point, Ruiteinberg [29] and Soliman [30] have derived the Kissinger Equation by integrating the DSC signal formula [31, 32] and the defects reaction rate equation [1, 2, 31] which is believed to describe the glass transition phenomenon correctly. Ruiteinberg suggested that Kissinger method could be applied to the glass transition peak in amorphous metals. Furthermore, Soliman believed that the Kissinger plot is valid throughout the whole glass transition temperature range. However, Ruitenberg and Soliman had introduced many simplifications to achieve

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the Kissinger equation without giving clear scientific reasons, which led to their conclusions being doubtful. Thus, it is interesting to investigate what can be attained if no simplification was proposed, which has been done in this paper. The maximum rate equation during amorphous metals' structure relaxation is transformed into a Lambert W function. According to the new equation, the structure relaxation activation energy at DSC trace extreme points can be gained precisely through a numerical approach.

Theoretical background

The theoretical background used here can be also found in Ref. [29] and Ref. [30]. Structural defects were defined as local deviations from the ideal order [1]. Its concentration c has relation to the reduced free volume x [1, 2, 31] as below [33]

$$c = \exp(-1/x) \tag{1}$$

In equilibrium, the defect concentration depends on temperature T through $c_e = \exp[-B/(T - T_0)]$ [33], where $x_e \equiv (T - T_0)/B$ is the equilibrium reduced free volume; T_0 and B are constants of unit K. Note that when $T \gg T_0$, C_e has the mathematical form of a Boltzmann fraction, with $k_B B$(where k_B is the Boltzmann constant) as the activation energy for the formation of the structural defects [29]. When the defect concentration is not in equilibrium, it will approach the equilibrium value. In that case, the rate of change of the defect concentration equals to [31, 34]

$$dc/dt = -kc(c - c_e) \tag{2}$$

The rate constant k has an Arrhenius temperature dependence $k = k_0 \exp[-E/(k_B T)]$, where E is the activation energy for the migration of the structural defects and k_0 is a constant of unit per second.

In DSC test, the variation of chemical order as well as that of free volume contribute to the signal [29, 31, 32], which can be described as:

$$dH/dt = \alpha dx/dt + \beta d\psi/dt. \tag{3}$$

Here, H is the internal free energy related to structure. ψ represents the chemical order of the processes. α and β are constants. Sietsma and van den Beukel have concluded that the basic features of the glass transition observed in DSC can be associated mainly with the changes of the free volume, so the chemical order term in Eq. 3 can be neglected [31, 32].

Mathematical treatment

Substituting with Eq. 1, Eq. 2 can be rewritten into the following form.

$$dx/dt = -kx^2(c - c_e). \tag{4}$$

When the sample was heated at a constant rate φ, the temperature could be expressed as $T = \varphi t + T_i$. T_i is the initial temperature, which is often room temperature. Substituting t with T in Eq. 4 gives

$$dx/dT = -kx^2(c - c_e)/\varphi \tag{5}$$

At the extreme points of the DSC trace,such as the onset temperature and the peak temperature of glass transition [35], the relation below is satisfied

$$d^2x/dt^2 = 0 \tag{6}$$

or

$$d^2x/dT^2 = \varphi^{-2} d^2x/dt^2 = 0 \tag{7}$$

First, it is assumed that the activation energy is independent on temperature, so the differential coefficient of Eq. 5 with respect to temperature could be obtained.

$$d^2x/dT^2 = -\left\{Ex^2(c - c_e)/k_B T^2 - Bc_e x^2 \Big/ (T - T_0)^2 + [2x(c - c_e) + c]dx/dT\right\} k \Big/ \varphi \tag{8}$$

Thus, when Eq. 5 is substituted into Eq. 8 and set to zero, we have

$$E/(k_B T) - BTc_e(T - T_0)^{-2}(c - c_e)^{-1} = k_0 T[2x(c - c_e) + c]e^{-E/(k_B T)} \Big/ \varphi. \tag{9}$$

Then, if we define

$$E/(k_B T) \equiv \gamma_1 \tag{10a}$$

$$BTc_e(T - T_0)^{-2}(c - c_e)^{-1} \equiv \gamma_2 \tag{10b}$$

$$k_0 T[2x(c - c_e) + c]/\varphi \equiv \gamma_3 \tag{10c}$$

Eq. 9 can be revised as follows:

$$(\gamma_1 - \gamma_2)e^{(\gamma_1 - \gamma_2)} = \gamma_3 e^{-\gamma_2} \tag{11}$$

which is Lambert W function [36].

In mathematics, Lambert's W function, named after Johann Heinrich Lambert, also called the Omega function, is the inverse function of $y = w \cdot e^w$ for complex numbers w; Since y is not injective, w is multivalued (except at 0). Fortunately, the function has single real solution for $y \geq 0$ [36]. In Eq. 11, $\gamma_3 e^{-\gamma 2}$ composes the y term above, it's sign is determined only by γ_3 for that $f(z) = e^z$ is positive forever. Because excessive free volume annihilates until that glass transition occurs when the sample is heated, x is larger than x_e, which make term $c - c_e$ in Eq. 10c is positive. Furtherly, γ_3 is positive according to Eq. 10c, so the solution of Eq. 11 is single real, and the γ_1 in Eq. 11 can be expressed as follow by *Lambertw* symbol

$$\gamma_1 = Lambertw(\gamma_3 e^{-\gamma_2}) + \gamma_2 \quad (12)$$

which can be calculated through Matlab7.0 software directly using the *lambertw*(X) syntax when γ_2 and γ_3 are known. Consequently, the glass transition activation energy could be obtained from Eq. 12.

In order to investigate the relationship between the glass transition activation energy and the state of the sample, a parameter of η is introduced as the ratio of x to x_e.

$$\eta = x/x_e \quad (13)$$

η represents the extent that sample approaches equilibrium state at a certain temperature for two reasons. First, the annihilation and production of defects during structure relaxation should end when x reaches x_e, because equilibrium is considered as a stable state or metastable state. Second, the actual thermally activated transformation processes of alloys cannot fully reach the state of equilibrium.

Glass transition activation energy of $Pd_{40}Ni_{40}P_{20}$

Structure relaxation of $Pd_{40}Ni_{40}P_{20}$ amorphous alloy in as-quenched state has been investigated. The parameters B, T_0 and k_0 are shown in Table 1 [2]. Table 2 shows the glass transition temperatures and corresponding heating rates, these data were got from the DSC tests [35].

Based on the data in Tables 1 and 2, the glass transition activation energy of $Pd_{40}Ni_{40}P_{20}$ alloy in a quenched state is plotted versus parameter η in Fig. 1, where η is larger than 1.0, for excessive free volume annihilates until that glass transition occurs when the sample is heated.

Table 1 Parameters for calculating glass transition peak activation energy of $Pd_{40}Ni_{40}P_{20}$ [2]

Parameters	Values	Units
B	6,600	K
T_0	355	K
k_0	3.4×10^{25}	Hz

Table 2 Glass transition temperatures and corresponding heating rates determined in DSC experiments of as-cast $Pd_{40}Ni_{40}P_{20}$ alloy [35]

φ (Ks^{-1})	T_g (K)
0.059	563
0.201	570
0.374	574
0.698	577
1.442	581

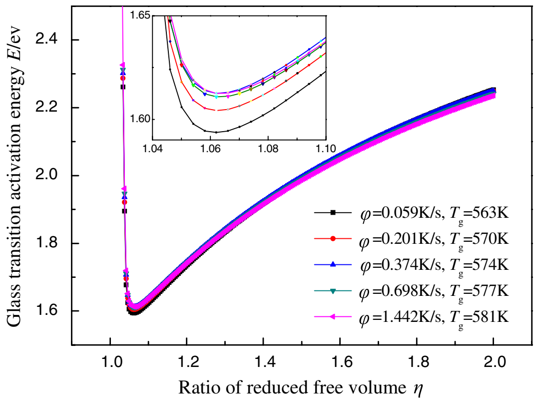

Fig. 1 Glass transition activation energy of as-cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy versus the ratio of reduced free volume. φ denotes the heating rate and T_g is glass transition temperature

Obviously, E is influenced by η. Figure 1 indicates that the glass transition energy of the quenched $Pd_{40}Ni_{40}P_{20}$ amorphous alloy decreases to its minimum, and then increases to infinite when x approaches x_e, which means the relaxation cannot fully reach the state of equilibrium. At different heating rates, the activation energy traces in Fig. 1 differ little from each other and are minimally at the same ratio of reduced free volume, 1.0621, where the glass transition activation energies for the five heating rates are 1.5936, 1.6043, 1.6126, 1.6109 and 1.6126 eV, respectively. It has been mentioned in the introduction that assumption of equivalent fraction transformed (also called fixed or identical stage) which may be defined as the stage at which a fixed amount is transformed, or at which a fixed fraction of the total amount is transformed for various heating rates [17], was applied in isoconversion methods. However, in some cases, the equivalent stage assumption may not hold and this introduces deviations in the measured activation energies [9, 17, 25]. Here, the result shows that the ratio of reduced free volume is fixed. The glass transition temperatures are different for various heating rates, the equilibrium reduced free volumes also differ each other, so the reduced free volumes of glass transition are different for various heating rates.

As thermally activated reactions, the atoms' colliding and rearranging during structure relaxation cause that the free volume annihilates and produces [37, 38], which bears an analogy to usual chemical reactions in which the reactant molecules collide, rearrange and then come to product molecules. This analogy is also shown from that structure relaxation and chemical reactions bear similar kinetic rate equation. Therefore, it would be reasonable to assume that the kinetic properties during structure relaxation in amorphous metals obey the theories of chemical reactions. Thus, the structure relaxation would process along the reaction path of minimum activation energy.

According to Fig. 1, the glass transition activation energy of $Pd_{40}Ni_{40}P_{20}$ amorphous alloy in as-quenched state is 1.6 eV, which is close to the result in Ref. [2] where the glass transition activation energy of as-cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy was fitted through viscosity measurements in the glass transition zone and the value is 1.7 eV. The difference, 0.1 eV, may come from that the latter is the average of the activation energy during structure relaxation.

The glass transition activation energy of $Pd_{40}Ni_{40}P_{20}$ amorphous alloy in as-quenched state also be calculated using the Kissinger method, FWO method and Starink II method according to the data shown in Table 2. The results are listed comparing with the results obtained through the new method and through viscosity measurements, see Table 3.

Shown in Table 3, the glass transition activation energies evaluated with the Kissinger method [16], FWO method [39] and Starink II [17] are higher than that calculated with the new method and with viscosity measurements. As is well known in conversion methods like the Kissinger method suppose that a constant amount transformed fraction was achieved at the characteristic temperatures when the material was heated at different rates. However, the amount transformed always varies at different heating rates, which would inevitably introduce errors. Moreover, Tuinstra [31] has pointed out the Kissinger analysis cannot be used to calculate the activation energy of the non-first-order rate process like that of the $Pd_{40}Ni_{40}P_{20}$ amorphous alloy. However, the viscosity measurement method has been widely used to study the structure relaxation of materials, and the result gained from viscosity measurement should be more credible. Thus, the glass transition activation energy of the quenched $Pd_{40}Ni_{40}P_{20}$ amorphous alloy processed with Lambert W function in this paper is reasonable.

Parameter sensitivity analysis

The parameters B, k_0 and T_0 used in the calculation above were obtained from the viscosity measurements of as-cast

Table 3 Activation energy calculated with different methods for as cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy

Methods	Activation energy (eV)	Formula
New	1.6	$\gamma_1 = Lambertw(\gamma_3 e^{-\gamma_2}) + \gamma_2$
Viscosity measurements	1.7	–
Kissinger	4.9	[16] $\ln\left(\varphi / T_g^2\right) = -E/(K_B T_g) + C$
Flynn–Wall–Ozawa	4.7	[39] $\ln \varphi = -1.0516E/(K_B T_g) + C$
Starink II	4.8	[17] $\ln\left(\varphi / T_g^{1.92}\right) = -1.008E/(K_B T_g) + C$

Table 4 The glass transition activation energy of as-cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy calculated under different values of the parameters B, T_0 and k_0

Parameters			E (ev)					η
B (K)	T_0 (K)	k_0 (Hz)	$\varphi = 0.059$ K/s, $T_g = 563$ K	$\varphi = 0.201$ K/s, $T_g = 570$ K	$\varphi = 0.374$ K/s, $T_g = 574$ K	$\varphi = 0.698$ K/s, $T_g = 577$ K	$\varphi = 1.442$ K/s, $T_g = 581$ K	
6600	355	3.4×10^{25}	1.5936	1.6043	1.6126	1.6109	1.6126	1.0621
6700	355	3.4×10^{25}	1.5716	1.5827	1.5913	1.5897	1.5916	1.0621
6500	355	3.4×10^{25}	1.6157	1.6259	1.6341	1.6321	1.6336	1.0621
6400	355	3.4×10^{25}	1.6387	1.6488	1.6555	1.6533	1.6546	1.0621
6300	355	3.4×10^{25}	1.6600	1.6693	1.6769	1.6746	1.6756	1.0621
6800	355	3.4×10^{25}	1.5495	1.5611	1.5699	1.5685	1.5707	1.0621
6600	200	3.4×10^{25}	2.2006	2.1869	2.1821	2.1706	2.1599	1.0501
6600	250	3.4×10^{25}	2.0700	2.0601	2.0574	2.0475	2.0388	1.0541
6600	300	3.4×10^{25}	1.8902	1.8868	1.8877	1.8804	1.8751	1.0581
6600	400	3.4×10^{25}	1.2058	1.2403	1.2611	1.2684	1.2816	1.0661
6600	450	3.4×10^{25}	0.4491	0.5430	0.5948	0.6244	0.6654	1.0782
6600	355	2.5×10^{25}	1.5796	1.5901	1.5983	1.5965	1.5981	1.0621
6600	355	3.0×10^{25}	1.5879	1.5985	1.6068	1.6050	1.6067	1.0621
6600	355	4.0×10^{25}	1.6011	1.6118	1.6202	1.6185	1.6202	1.0621
6600	355	4.5×10^{25}	1.6065	1.6173	1.6257	1.6240	1.6258	1.0621
6600	355	5.0×10^{25}	1.6113	1.6222	1.6306	1.6289	1.6308	1.0621

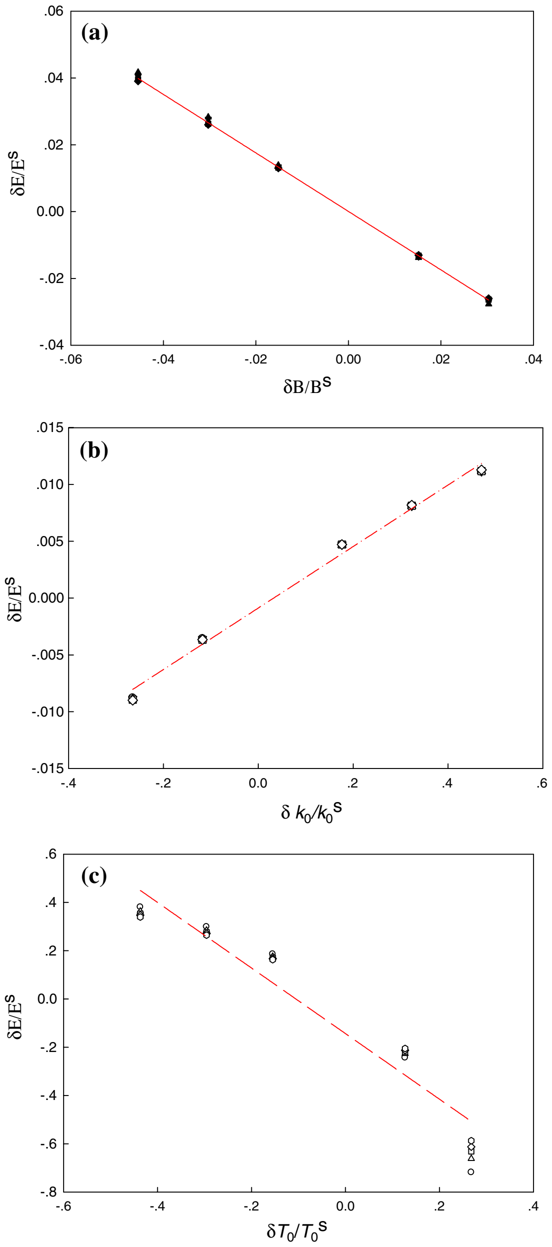

Fig. 2 The sensitivity plots of the relative variation of the activation energy to the relative variation of the parameters. **a** B, **b** k_0 and **c** T_0

$Pd_{40}Ni_{40}P_{20}$ amorphous alloy in the glass transition zone, so the error may generate inevitably, which have been shown in Ref. [2]. On the other hand, because the viscosity measurements are quite tedious, it is necessary to develop some convenient methods to evaluate the parameters, however, convenience may decrease the precision of the parameters. Thus, the effect of the precision of the parameters B, k_0 and T_0 on the results calculated with the Eq. 12 should be explored. To achieve this aim, the glass transition activation energy of as-cast $Pd_{40}Ni_{40}P_{20}$ amorphous alloy was calculated under different values of the parameters above, the results were listed in Table 4. The results obtained under $B = 6600$ K, $T_0 = 355$ K, $k_0 = 3.4 \times 10^{25}$Hz also be listed in it.

It is indicated that the variation of the parameters cannot change the glass transition activation energy largely, and the ratio of reduced free volume corresponding to the glass transition shifted tinily. In statistics, the sensitivity of a model $F = f(x_1, x_2, x_3 \ldots x_n)$ to the parameter x_i in the neighbourhood of a reference sample can be described quantitatively with the sensitivity coefficient S_i, which is defined as the absolute value of the slope of the relative variation of the activation energy with respect to the relative variation of the parameters [40].

$$S_i = \left| \frac{d(\delta F / F^s)}{d(\delta x_i / x_i^s)} \right| \tag{14}$$

where F^s and x_i^s compose the reference sample, $F^s = f\left(x_1^s, x_2^s, x_3^s \ldots x_i^s \ldots x_n^s\right)$. According to Table 4, the sensitivity plots of the relative variation of the activation energy to the relative variation of the parameters are figured (Fig. 2). We can see that the relative variation of the activation energy is related linearly to the relative variation both of B and k_0, but to the relative variation of T_0 that relation is not strict hold. Fitting the data gets the absolute values of the slope of them are 0.8759, 0.0271 and 1.3588, respectively, thus, the method is sensitive most to the parameter $T_{0,}$ and not sensitive to k_0, which means that the parameter T_0 should be determined more strictly.

In this analysis, the changes of the parameters are very large, which occurs barely in actual measurements or evaluation. Even under large changes, the variation of the activation energy is small enough to avoid intrinsic mistakes, so we can believe that errors in determination of the parameters is concessional at large extent.

Conclusions

The new approach with the Lambert W function to calculate the structure relaxation activation energy at the glass transition points on DSC trace was derived. Based on this method, the glass transition activation energy of the $Pd_{40}Ni_{40}P_{20}$ amorphous alloy in as-quenched state was evaluated and the result agreed well with that obtained through viscosity measurements. Thus, there is a good possibility that the new approach is an applicable and simple method to estimate structure relaxation activation energy. We can employ it when the necessary parameters are known. In this paper, the parameters are fitted from viscosity measurements. A simpler route should be investigated in future.

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Appendix

The M-file of Matlab 7.0 for calculating the activation energy in this paper

```
B=6600;                                              %Define the basic parameters
T0=355;
k=3.4*10^25;
kb=1.38*10^(23);
h=linespace(1,2,500);                                %Define the argument η as h and its zone for calculation
fi=0.059;                                            %Define the heating rate φ as fi and assign it's value
Tg=563;                                              %Define the temperature of glass transition Tg and assign it's value
xe=(Tg−T0)/B;                                        %Calculating the equilibrium reduced free volume
for i=1:500                                          %The loop for calculating the glass transition activation energy E of the
                                                       first DSC test
e=exp((1−1/h(i))/xe);
r2=Tg/(Tg−T0)/xe/(e−1);                              %Calculating γ2
r3=xe*exp(−1/xe)*k*Tg/fi*(2*h(i)*(e−1)+e);           %Calculating γ3
r=r3*exp(−r2);
E1(i)=(lambertw(r)+r2)*kb*Tg/1.6*10^19;              %Calculating E and change the unit into eV
end
fi=0.201;                                            %The loop for calculating the glass transition activation energy E
                                                       of the second DSC test
Tg=570;
xe=(Tg−T0)/B;
for i=1:500
e=exp((1−1/h(i))/xe);
r2=Tg/(Tg−T0)/xe/(e−1);
r3=xe*exp(−1/xe)*k*Tg/fi*(2*h(i)*(e−1)+e);
r=r3*exp(−r2);
E2(i)=(lambertw(r)+r2)*kb*Tg/1.6*10^19;
end
fi=0.374;                                            %The loop for calculating the glass transition activation energy E
                                                       of the third DSC test
Tg=574;
xe=(Tg−T0)/B;
for i=1:500
e=exp((1−1/h(i))/xe);
r2=Tg/(Tg−T0)/xe/(e−1);
r3=xe*exp(−1/xe)*k*Tg/fi*(2*h(i)*(e−1)+e);
r=r3*exp(−r2);
E3(i)=(lambertw(r)+r2)*kb*Tg/1.6*10^19;
end
fi=0.698;                                            %The loop for calculating the glass transition activation energy E
                                                       of the fourth DSC test
Tg=577;
xe=(Tg−T0)/B;
for i=1:500
e=exp((1−1/h(i))/xe);
r2=Tg/(Tg−T0)/xe/(e−1);
r3=xe*exp(−1/xe)*k*Tg/fi*(2*h(i)*(e−1)+e);
r=r3*exp(−r2);
E4(i)=(lambertw(r)+r2)*kb*Tg/1.6*10^19;
end
```

continued

```
fi=1.442;                                                  %The loop for calculating the glass transition activation energy E
                                                             of the fifth DSC test
Tg=581;
xe=(Tg−T0)/B;
for i=1:500
e=exp((1−1/h(i))/xe);
r2=Tg/(Tg−T0)/xe/(e−1);
r3=xe*exp(−1/xe)*k*Tg/fi*(2*h(i)*(e−1) + e);
r=r3*exp(−r2);
E5(i)=(lambertw(r)+r2)*kb*Tg/1.6*10^19;
end
plot(h,real(E1),h,real(E2),h,real(E3),h,real(E4),h,real(E5))
xlabel(Ratio of reduced free volume η)
ylabel(Activation energy E(eV))
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References

1. Spaepen F. Defects in amorphous metals. In: Balian R, editor. Les Houches lectures XXXV on physics of defects. North Holland: Amsterdam; 1981, p. 136–74.
2. Duine PA, Sietsma J, van den Beukel A. Defect production and annihilation near equilibrium in amorphous $Pd_{40}Ni_{40}P_{20}$ investigated from viscosity data. Acta Metallurgica et Materialia. 1992;40(4):743–51.
3. Freeman ES, Carroll B. The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J Phys Chem. 1958;62(4):394–7.
4. Achar BN, Sharp JH, Sharp JH. Thermal decomposition kinetics of some new unsaturated polyesters. In: Heller L, Weiss A, editors. Proceedings of the international clay conference. Jerusalem: 1966.
5. Chatterjee PK. Application of thermogravimetric techniques to reaction kinetics. J Polym Sci A. 1965;3(12):4253–62.
6. Ortega A. The incorrectness of the temperature criterion. Thermochim Acta. 1996;276:189–98.
7. Serra R, Sempere J, Nomen R. A new method for the kinetic study of thermoanalytical data: the non-parametric kinetics method. Thermochim Acta. 1998;316(1):37–45.
8. Serra R, Nomen R, Sempere J. The non-parametric kinetics a new method for the kinetic study of thermoanalytical data. J Therm Anal Cal. 1998;52(3):933–43.
9. Gao Z, Nakada M, Amasaki I. A consideration of errors and accuracy in the isoconversional methods. Thermochim Acta. 2001;369(1–2):137–42.
10. Lopez-alemany PL, Vazquez J, Villares P, Jimenez-garay R. A kinetic study on non-isothermalcrystallization of the glassy alloy $Sb_{0.16}As_{0.43}Se_{0.41}$. J Non-Cryst Solids Phys Non-Cryst Solids Phys Non-Cryst Solids. 2000;274(1–3):249–56.
11. Li CR, Tang TB. A new method for analysing non-isothermal thermoanalytical data from solid-state reactions. Thermochim Acta. 1999;325(1):43–6.
12. Starink MJ. A new method for the derivation of activation energies from experiments performed at constant heating rate. Thermochim Acta. 1996;288(1–2):97–104.
13. Mittemeijer EJ. Analysis of the kinetics of phase transformations. J Mater Sci. 1992;27:3977–87.
14. Matusita K, Komatsu T, Yokota R. Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials. J Mater Sci. 1984;19(1):291–6.
15. Dragoe N, Segal E. Pseudo-inverse matrix method – a direct method for non-isothermal kinetic analysis. J Therm Anal Cal. 1998;54(3):931–5.
16. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29(11):1702–6.
17. Starink MJ. The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. Thermochim Acta. 2003;404(1–2):163–76.
18. Vyazovkin S. Advanced isoconversional method. J Therm Anal. 1997;49(3):1493–9.
19. Vyazovkin S, Dollimore D. Linear and nonlinear procedures in isoconversional computations of the activation energy of non-isothermal reactions in solids. J Chem Inf Comput Sci. 1996;36(1):42–5.
20. Criado JM, Ortega A, Gotor F. Correlation between the shape of controlled-rate thermal analysis curves and the kinetics of solid-state reactions. Thermochim Acta. 1990;157(1):171–9.
21. Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochim Acta. 1999;341(Sp. Iss. SI):53–68.
22. Criado JM, Gonzalez M, Ortega A, Real C. Some considerations regarding the determination of the activation energy of solid-state reactions from a series of isothermal data. J Thermal Anal. 1984;29(2):243–50.
23. Ortega A. The kinetics of solid-state reactions toward consensus, Part 2: fitting kinetics data in dynamic conventional thermal analysis. Int J Chem Kinet. 2002;34(3):193–208.
24. Vyazovkin S. Thermal analysis. Anal Chem. 2004;76(12):3299–311.
25. Starink MJ. On the applicability of isoconversion methods for obtaining the activation energy of reactions within a temperature-dependent equilibrium state. J Mater Sci. 1997;32(24):6505–12.
26. Wang HR, Gao YL, Ye YF, Min GH, Chen Y, Teng XY. Crystallization kinetics of an amorphous Zr-Cu-Ni alloy: calculation of the activation energy. J Alloy Compd. 2003;353(1–2):200–6.
27. Yamada K, Ito M, Tatsumiya M, Lijima Y, Fukamichi K, editors. Activation energy for the structural relaxation process of amorphous Tb-Fe and Tb-Fe-Si alloys. Proceedings of the fifth

international conference on diffusion in materials (DIMAT 2000). Paris, France: Trans Tech Publications Ltd; 2001.

28. Ye F, Lu K. Crystallization kinetics of Al-La-Ni amorphous alloy. J Non-Cryst Solids. 2000;262(1):228–35.
29. Ruitenberg G. Applying Kissinger analysis to the glass transition peak in amorphous metals. Thermochim Acta. 2003;404(1–2):207–11.
30. Soliman A. Derivation of the Kissinger equation for non-isothermal glass transition peaks. J Therm Anal Cal. 2007;89(2):389–92.
31. Tuinstra P, Duine PA, Sietsma J, van den Beukel A. The calorimetric glass transition of amorphous $Pd_{40}Ni_{40}P_{20}$. Acta Metallurgica et Materialia. 1995;43(7):2815–23.
32. Van B, Sietsma J. The glass transition as a free volume related kinetic phenomenon. Acta Metall. 1990;38(3):383–9.
33. Cohen MH, Turnbull D. Molecular transport in liquids and glasses. J Chem Phys. 1959;31(5):1164–9.
34. Tsao SS, Spaepen F. Structural relaxation of a metallic glass near equilibrium. Acta Metall. 1985;33(5):881–9.
35. Sinning HR, Haessner F. Comparison of damping measurement and differential scanning calorimetry as methods of determining the glass transition temperature in metallic glasses. Mater Sci Eng. 1988;97:453–6.
36. Corless R, Gonnet G, Hare D, Jeffrey D, Knuth D. On the Lambertw function. Adv Comput Math. 1996;5(1):329–59.
37. Koebrugge GW, Sietsma J, Van BA. Structural relaxation in amorphous $Pd_{40}Ni_{40}P_{20}$. Acta Metallurgica et Materialia. 1992;40(4):753–60.
38. Hammond VH, Houtz MD, O'Reilly JM. Structural relaxation in a bulk metallic glass. J Non-Cryst Solids. 2003;325(1–3):179–86.
39. Flynn JH, Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. J Polym Sci B. 1966;4(5):323–8.
40. Saltelli A, Tarantola S, Campolongo F. Sensitivity analysis as an ingredient of modelling. Stat Sci. 2000;15:377–415.