Calculation of Supercooled Liquid Range and Estimation of Glass-Forming Ability of Metallic Glasses using the Vogel-Fulcher-Tammann Equation

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The supercooled liquid range (ΔT_x) was calculated on the basis of the free volume theory proposed by Beukel and Sietsma. A differential equation which expresses the change in free volume from a non-equilibrium to an equilibrium state has been analyzed numerically for Ni, metallic glasses and SiO_2 systems. The Vogel-Fulcher-Tammann (VFT) equation for viscosity was used to define the equilibrium free volume. The maximum ΔT_x was calculated as 56 K for the SiO_2 system. The calculated ΔT_x was approximately six times smaller than the experimental result. The calculation results of the $\log R_c$ (R_c : critical cooling rate for glass formation)- ΔT_x diagram shows a tendency similar to the experimental result; $\log R_c$ decreases linearly with increasing ΔT_x . An approximate solution of the differential equation was also obtained with elementary functions. It was found that the glass transition temperature (T_g) and ΔT_x can be obtained schematically in the free-volume-temperature diagram. All the factors expressing the glass-forming ability of the metallic glasses can be derived from the VFT parameters.

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1. Introduction

Since the first successful preparation of an amorphous phase in an Au-Si system in 1960,¹⁾ a great number of amorphous alloys have been found. Some of the amorphous alloys which exhibit the glass transition phenomena are classified as metallic glasses according to the scientific definition. Recently, a number of metallic glasses have been found in special multicomponent systems²⁾ in which the nucleation and growth reactions of a crystalline phase are suppressed. These metallic glasses exhibit similar unique characteristics to those found among the amorphous alloys in terms of their physical, chemical, mechanical, and magnetic properties. However, a significant difference has been discerned in their thermal properties. That is, the metallic glass, when subjected to continuous heating exhibits the glass transition temperature (T_g), and then transforms into a large supercooled liquid.

The glass-forming ability (GFA) is generally indicated by the minimum cooling rate to avoid the nucleation and growth of crystals during continuous cooling from the melted state. In fact, this parameter is also applicable to the amorphous alloys because both the amorphous alloys and metallic glasses vitrify into a non-crystalline state by the mechanism described above. Accordingly, the GFA has been practically estimated using the following three factors:²⁾ (1) reduced glass transition temperature (T_g/T_m), (2) supercooled liquid range ΔT_x ($= T_x - T_g$), and (3) critical cooling rate (R_c) for formation of the glassy phase. The first two factors are determined from the following three temperatures which are measured by thermal analysis, *i.e.*, the glass transition temperature (T_g), melting temperature (T_m), and onset temperature of crystallization (T_x). On the basis of the experimental results, the dominant factors for GFA are summarized in the $R_c - T_g/T_m$ and $R_c - \Delta T_x$ diagrams.²⁾ These diagrams indicate that the metallic glasses with high GFA have the following threshold values for the GFA factors: $R_c \leq 10^5$ K/s, $T_g/T_m \geq 0.6$ and $\Delta T_x \geq 50$ K.

In addition to the experimental studies on the GFA factors for metallic glasses, a number of theoretical studies have been carried out to evaluate the R_c ³⁻¹⁴⁾ and to clarify the relation between R_c and T_g/T_m .^{4,6,13)} The GFA factors have been recently summarized^{15,16)} for typical metallic glasses by combining the theoretical R_c with the experimental results of T_g/T_m and ΔT_x . To our knowledge, however, the relationship among all the GFA factors have not been analyzed theoretically in the framework of a general model.

We have thus started to establish the general models for analyzing the quantities of the metallic glasses from a theoretical point of view. As a result, we have succeeded in deriving a relationship corresponding to the experimental result of $R_c - T_g/T_m$ from a time-transformation diagram¹⁷⁾ which expresses the crystallization of metallic glass. It should be noted that to calculate the transformation diagram only two necessary parameters are necessary: the Vogel-Fulcher-Tammann (VFT) equation for viscosity and the melting temperature (T_m). It is also important to note that the factor T_0/T_m (T_0 : ideal glass transition temperature) can be substituted for T_g/T_m in order to avoid the difficulty in analyzing the T_g which varies with the heating rate. This substitution of the factor implies the conversion of a variable from a kinetic to a thermodynamic transformation temperature (T_g to T_0).

If the $R_c - \Delta T_x$ diagram is studied carefully, it becomes apparent that there is a problem because the ΔT_x cannot be calculated with equilibrium thermodynamic functions. The problem arises from the ΔT_x being defined by T_x and T_g ; since they are both kinetic transformation temperatures. Consequently, Beukel and Sietsma¹⁸⁾ analyzed the glass transition phenomenon on the basis of the change in free volume. In this study, an equilibrium free volume is defined by B and T_0 in the VFT equation for viscosity, and then the change in free volume from a non-equilibrium to an equilibrium state is numerically analyzed on the basis of a non-linear differential equation. As a result of this analysis, the glass transition of metallic glasses is described quantitatively under the condi-

tions where the experimental thermal analyses are made at a constant heating rate.¹⁸⁾

In accordance with the above-described model, we can calculate the ΔT_x by solving the differential equation using the VFT parameters for viscosity. Furthermore, we can analyze theoretically all the GFA factors and their relationship by combining them with the previous result¹⁷⁾ of $R_c - T_g/T_m$ which was calculated with the same VFT parameters. However, analyzing the differential equation frequently causes the following problems. For instance, it is difficult to obtain general solutions from the non-linear differential equation. Furthermore, the calculation process must suppress overshooting by using appropriate time intervals. Therefore, more efficient approaches for calculating the ΔT_x are needed in order to avoid these problems, *e.g.*, by a method of obtaining the approximate solution from the differential equation.

This paper has the following four purposes: (1) to calculate the ΔT_x by solving the differential equation in accordance with the method developed by Beukel and Sietsma, (2) to establish the $R_c - \Delta T_x$ diagram for typical metallic glasses found to date, (3) to derive an approximate solution from the differential equation, and (4) to clarify the relationship between the VFT parameters and the set of factors (R_c , T_g/T_m and ΔT_x) which are used for estimating the GFA of metallic glasses.

2. Calculation Method

The calculation method of ΔT_x for metallic glasses followed the method previously devised by Beukel and Sietsma.¹⁸⁾

First, the equilibrium free volume (x_{eq}) is defined by eq. (1) with B and T_0 of the VFT parameters:

$$x_{eq} = \frac{T - T_0}{B}. \quad (1)$$

Equation (1) is related to equilibrium viscosity (η_{eq}),

$$\eta_{eq} = \eta_0 \exp\left(\frac{B}{T - T_0}\right) = \eta_0 \exp(x_{eq}^{-1}), \quad (2)$$

expressed by the VFT equation for viscosity. In the calculation, the free volume (x) and x_{eq} are essentially converted to flow defect concentration (C_f) and equilibrium concentration (C_{fe}), respectively, with the following definitions,¹⁸⁾

$$\begin{aligned} C_f &= \exp\left(-\frac{1}{x}\right), \\ C_{fe} &= \exp\left(-\frac{1}{x_{eq}}\right). \end{aligned} \quad (3)$$

Then, the dx/dT is assumed¹⁸⁾ to be proportional to the specific heat ($(\Delta C_p)_{fv}$): $(\Delta C_p)_{fv} \propto dx/dT$.

Equation (4) shows the differential equation which describes the kinetic behavior of the free volume from a non-equilibrium to an equilibrium state:

$$\frac{dC_f}{dt} = -kC_f(C_f - C_{fe}), \quad (4)$$

where k is the rate constant, which is expressed by Arrhenius

formula shown in eq. (5),

$$k = C_0 \exp(-E_f/RT), \quad (5)$$

with the activation energy (E_f) and pre-exponential constant (C_0). The E_f and C_0 used in the present calculation were 160 kJ/mol and $2.1 \times 10^{23} \text{ s}^{-1}$, respectively, which are the same as those used in a previous study.¹⁸⁾

By solving eq. (4) under a constant heating rate, we can obtain the temperature dependence of x as illustrated in Fig. 1(a).¹⁸⁾ The dx/dT profile shown in Fig. 1(b) is assumed to hold the relation $(\Delta C_p)_{fv} \propto dx/dT$ in the temperature range from C to F denoted in Fig. 1(a). On the basis of Figs. 1(a) and (b), Beukel and Sietsma defined the T_x and T_g as follows: the metallic glass crystallizes at F, and the glass transition occurs in the curve DEF where the dx/dT exhibits a sharp rise, *e.g.*, at E.

Equation (4) indicates that the kinetic process of C_f can be divided into three stages. The first stage is the region where $C_{fe} \ll C_f$; the C_f decreases with the reaction of the second order. The second stage coincides with the point D in Fig. 1(a), where the rate of the change in C_f is apparently zero because of $C_{fe} = C_f$. The final stage is a high temperature range corresponding to the curve DEF where $C_f < C_{fe}$. At the final stage, the $(C_f - C_{fe})$ term of eq. (4) becomes negative, giving an increase in C_f . One can calculate the time evolution of C_f by eq. (4) with the constants E_f , C_0 , x_0 , B and T_0 . In the present study, heating rate is fixed at 0.67 K/s.

The critical cooling rate for formation of a glassy phase (R_c) was taken from our previous results¹⁷⁾ calculated from an isothermal transformation diagram which expresses the crystallization of metallic glasses. In this study, the following equation is proposed from Davies's equation⁴⁾ to describe the

Fig. 1 Schematic diagrams showing the changes in (a) free volume (x) and (b) dx/dT with temperature of a metallic glass during rapid quenching (A to C) and subsequent continuous heating (C to F).¹⁸⁾ B: VFT parameter, T_0 : ideal glass transition temperature, T_g : glass transition temperature, T_x : onset temperature of crystallization, T_f : fictive temperature, x_0 : initial free volume, x_{eq} : equilibrium free volume.

transformation curve (C-curve):

$$t = \left[\frac{31}{k_B} \left(\frac{X a_0^9}{N_v} \right)^{1/4} \right] \times \left[\frac{1}{T_r \Delta T_r^{3/4}} \exp \left(\frac{0.268}{T_r^3 \Delta T_r^2} \right) \exp \left\{ \frac{2}{5} \left(\frac{T_r}{\Delta T_r} \right)^{3/4} \right\} \right] \times \left[\eta_{0r} \exp \left(\frac{B_r}{T_r - T_{0r}} \right) \right]. \quad (6)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, X is the fraction of crystal formed in time t , a_0 is the mean atomic diameter, and N_v is the volume concentration of atoms. The $T_r (= T/T_m)$ is the reduced temperature defined by T normalized by melting temperature T_m , and $\Delta T_r (= 1 - T_r)$ is the reduced undercooling of the melt. The C-curve is then calculated in the $T - T_r - T$ diagram for metallic glasses where $X = 10^{-6}$, $a_0 = 0.226$ nm, and $N_v = 6.2 \times 10^{28}$ molecules/m³. In the calculation, the necessary parameters are as follows: reduced VFT parameters (η_{0r} , B_r , T_{0r}) which are the VFT parameters normalized by T_m . Then, the R_c is calculated by $R_c = R_{cr} \times T_m$ where R_{cr} (reduced critical cooling rate) is defined by the point of contact between the tangent of the C-curve and R_r in the $T - T_r - T$ diagram. The systems, and parameters used for the calculation^{2,4,12,13,19–21} and the calculated R_c ¹⁷ are summarized in Table 1.

3. Results

Figures 2(a) and (b) show the plots of x and dx/dT for a $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ system. The dx/dT exhibits tem-

Table 1 Representative metallic glasses found to date, Vogel-Fulcher-Tammann (VFT) parameters (B and T_0), and calculated R_c . The R_c was calculated from the time-transformation diagram which was obtained using the VFT parameters. The data for Ni and SiO₂ are shown for comparison.

Alloy	B/K	T_0/K	Ref.	R_c
Ni	4700	295		9.0×10^8
Fe ₈₃ B ₁₇	4630	638		2.3×10^6
Co ₇₅ Si ₁₅ B ₁₀	4190	675		7.5×10^5
Fe ₇₉ Si ₁₀ B ₁₁	4505	701		5.0×10^5
Fe ₈₀ P ₁₃ C ₇	4600	616		5.5×10^4
Ni ₇₅ Si ₈ B ₁₇	4280	670	4)	1.8×10^5
Pt ₆₀ Ni ₁₅ P ₂₅	3560	405		9.6×10^3
Pd ₈₂ Si ₁₈	3730	557		5.1×10^3
Ni _{62.4} Nb _{37.6}	5380	810		2.9×10^3
Pd _{77.5} Cu ₆ Si _{16.5}	3820	553		1.0×10^3
Pd ₄₀ Ni ₄₀ P ₂₀	3600	509		1.6×10^2
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	4135	447	2)	1.4×10^{-3}
Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5}	7431	413	13)	8.7×10^0
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	8444	372		1.3×10^1
Nd ₁₃ Fe ₇₉ B ₈	6587	500		6.4×10^2
Nd ₁₆ Fe ₇₆ B ₈	12700	340	12)	4.8×10^1
Mg ₆₅ Cu ₂₅ Y ₁₀	5746	260	19)	3.4×10^1
Mg ₆₅ Ni ₂₀ Nd ₁₅	1362.5	366.6	20)	1.8×10^{-3}
Mg ₆₅ Ni ₂₀ Nd ₁₅	24433	70		1.7×10^{-1}
SiO ₂	34548	526	21)	5.4×10^{-7}

perature dependence similar to that of the specific heat profile of the metallic glasses as illustrated in Fig. 1(b). On the basis of the definitions described in section 2, the T_x and T_g are determined as 638 and 660 K, respectively, and the resulting ΔT_x is calculated as 22 K. The T_x and T_g determined for this alloy are also shown in Fig. 2(b). From this figure, the dx/dT at T_x and T_g exactly corresponds to the value of $1/B$ which is equal to $1/B$ in accordance with the definition in eq. (1). The details of the T_g and T_x are also shown in Fig. 2(c).

Figure 3 shows the plots of dx/dT for Ni, metallic glasses (Fe₈₃B₁₇, Pd₄₀Cu₃₀Ni₁₀P₂₀, Mg₆₅Ni₂₀Nd₁₅, Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5}) and SiO₂ systems. The upward and downward pointing arrows show the T_g and T_x , respectively, and the resulting ΔT_x is 20 K for Ni, 7 K for Fe₈₃B₁₇, 11 K for Pd₄₀Cu₃₀Ni₁₀P₂₀, 50 K for Mg₆₅Ni₂₀Nd₁₅, 20 K for Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5}, and 56 K for the SiO₂ system. From this figure, it is apparent that the ΔT_x is independent of T_g , but depends on $1/B$ as well as the maximum value of

Fig. 2 Changes in (a), (c) free volume (x), and (b) dx/dT for $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ system.

Fig. 3 Plots of dx/dT for Ni, metallic glasses (Fe₈₃B₁₇, Pd₄₀Cu₃₀Ni₁₀P₂₀, Mg₆₅Ni₂₀Nd₁₅, Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5}) and SiO₂ systems.

Fig. 4 (a) Experimental data on the $R_c - \Delta T_x$ diagram for metallic glasses,²⁾ and (b) calculated data for Ni, metallic glasses and SiO_2 systems.

the dx/dT . This tendency implies that the ΔT_x is in proportion to B .

Figure 4(a) shows the $R_c - \Delta T_x$ diagram experimentally determined for several metallic glasses,²⁾ and Fig. 4(b) is the calculated results for Ni, the metallic glasses and SiO_2 systems. In Fig. 4(a), there is a linear relationship between $\log R_c$ and ΔT_x which can be expressed as $(\log R_c = 4.5 - \Delta T_x / 27)$ by the least-squares method. One can also see a similar relationship in Fig. 4(b), though some plots deviate from the line $(\log R_c = 6.0 - \Delta T_x / 4.5)$ obtained by the same method.

Another feature of the calculated $R_c - \Delta T_x$ diagram in Fig. 4(b) is that the calculated ΔT_x is smaller than the experimental result. For instance, ΔT_x of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy is calculated to be nearly ten times smaller than that in the experimental results, though the calculated R_c approximately agrees with the experimental result. On average, the values of ΔT_x in Fig. 4(b) are approximately six times smaller than that in the experimental results in Fig. 4(a).

4. Discussion

In this section, we will focus on the following points: (1) analysis of an approximate solution for the differential equation, (2) the reason for the discrepancy between the calculated and experimental ΔT_x , and (3) analysis of the relationship between the VFT parameters and the set of factors (R_c , T_g/T_m and ΔT_x) which are used for the estimation of GFA.

4.1 Analysis of an approximate solution for the differential equation

As shown in the previous section, the differential equation was analyzed numerically in order to obtain the temperature

dependence of x , and the resulting ΔT_x . In solving the differential equation, however, we often encounter some difficulties. For instance, appropriate time intervals must be selected during the calculation in order to prevent the calculation from overshooting, which leads to a prolonged calculation time. Furthermore, one must analyze the equations one by one for each metallic glass, indicating the difficulty of obtaining general solutions. In order to overcome these difficulties, we obtain the approximate solution of eq. (4).

Although eq. (4) is a form of the Bernoulli equation of which the solution is mathematically obtainable, one cannot obtain the solution of eq. (4) by the analysis method for the following three reasons. The first arises from the non-linearity of the differential equation, and the second results from the temperature dependence of k in eq. (5). The third reason originates from the coexistence of different types of temperature dependence of the terms: Arrhenius type for k , and the VFT type for C_{fe} . Accordingly, an approximate solution is obtained by assuming that the solution consists of two linear terms corresponding to the first and the third regions described in Section 2. These linear terms are separately analyzed as follows.

Equation (7) shows eq. (4) again with the expanded terms on the right-hand side:

$$\frac{dC_f}{dt} = -kC_f^2 + kC_{fe}C_f. \quad (7)$$

First, we focus on the first term on the right-hand side in order to obtain the approximate solution corresponding to the first

region. Ignoring the second term, we can write eq. (7) as,

$$\frac{1}{C_f^2} dC_f = -k dt. \quad (8)$$

Equation (8) expresses a decrease in C_f as well as x with time because of the relaxation of metallic glasses on heating. It is to be noted that eq. (8) is a linear differential equation which can generally be solved by the analysis method. The variation t is then converted to T^* ($= 1/T$) through T in order to integrate both sides of eq. (8). This is due to the previous results^{22,23} that eq. (5) can be expressed as $(dC_f/dt) = (dC_f/(dT))\alpha$. By designating α as a heating rate, we obtain the following equation from eq. (8):

$$\int \frac{1}{C_f^2} dC_f = C_0 \int \frac{\exp\left(-\frac{E_f}{R} T^*\right)}{T^{*2}} dT^*. \quad (9)$$

The T^{*2} term in the right-hand side of eq. (9) appears from the integrating factor when the variable T is converted to T^* ,

$$dT = -\frac{1}{T^{*2}} dT^*. \quad (10)$$

By integrating the right-hand side in eq. (9) with respect to T^* , we can obtain the time evolution of C_f as an infinite multinomial series.²⁴ However, the approximate solution as an infinite formula is not useful in the analysis of x . Therefore, we apply the following approximation to eq. (9),

$$C'_0 = C_0 T^{*2}, \quad (11)$$

in order to obtain the solution of eq. (9) as a single term integrand of the elementary functions. Here, C'_0 depends on C_0 as well as E_f of eq. (5). For the present calculation constants ($E_f = 160 \text{ kJ/mol}^{-1}$ and $C_0 = 2.1 \times 10^{23} \text{ s}^{-1}$), the value of C'_0 was obtained by the least-squares method as $C'_0 = 2.1 \times 10^{31} \text{ s}^{-1}$ which was approximated to fit k in eq. (5) at temperatures ranging from 0 to 2000 K. The validity for this approximation will be discussed later. Now, eq. (9) can be written as,

$$\int \frac{1}{C_f^2} dC_f = C'_0 \int \exp\left(-\frac{E_f}{R} T^*\right) dT^*, \quad (12)$$

which yields a linear solution of eq. (9):

$$C_f = \frac{C_{f0}}{\left\{ 1 + \frac{C'_0 R}{E_f \alpha} C_{f0} \exp\left(-\frac{E_f}{RT}\right) \right\}}. \quad (13)$$

Here, C_{f0} is the initial value of C_f (3.55×10^{-9}) calculated by eq. (3) with $x_0 = 0.0514$.

Second, the approximate solution corresponding to the third region is analyzed. This solution is another linear solution of eq. (7) in the higher temperature range. The solution is in the following form,

$$C_f = \exp\left(-\frac{B}{T - T_0}\right), \quad (14)$$

which is the concentration expression of x_{eq} . This is because the solution at $T \gg T_x$ follows C_{eq} (x_{eq}) as illustrated by the line AG in Fig. 1,

Having obtained the linear solutions of eq. (7) correspond-

ing to the first and the third region, we apply the final assumption that the approximate solution of eq. (7) is the sum of eqs. (13) and (14).

$$C_f = \frac{C_{f0}}{\left\{ 1 + \frac{C'_0 R}{E_f \alpha} C_{f0} \exp\left(-\frac{E_f}{RT}\right) \right\}} + \exp\left(-\frac{B}{T - T_0}\right). \quad (15)$$

Figure 5 shows, as before in Fig. 2, the plots of x and dx/dT for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, respectively, with the approximate solution (x_{ap}) calculated by eq. (15). From these figures, x_{ap} fits the solution numerically analyzed (x_{nu}) by eq. (4) in the temperature range of 300 to 800 K. This indicates that the value of C'_0 introduced thus is appropriately fitted for C_0 and E_f in eq. (5).

Figure 5(c) shows the temperature dependence of x_{ap} near T_g in more detail. From Fig. 5(c), T_g and ΔT_x can be obtained substitutionally from the following specific temperatures: $T_{trans,s}$ and $T_{trans,f}$. These temperatures are defined by the temperature where x_{ap} separates from a linear solution (x_{lin}) calculated by eq. (13), and where x_{ap} coincides with x_{eq} obtained by eq. (14), respectively. From the figure, T_x is obtained from x_{ap} because $T_{trans,f}$ exactly corresponds to T_x . However, T_g cannot be determined in x_{ap} for the following two reasons. First, x_{ap} does not cross x_{eq} , in disagreement with the definition of T_g described in Section 2. Second, the dx_{ap}/dT curve between T_g and T_x does not have the projection part which is a characteristic of metallic glass in the specific heat curve. Although it is impossible to determine T_g in x_{ap} , the cross-point (T_{cross}) between x_{lin} and x_{eq} is plotted just near T_g . By summarizing the above-described features of the specific temperatures, we can obtain the following estimations that ΔT_x is in proportion to ΔT_{trans} ($= T_{trans,f} - T_{cross}$), and that T_{cross} is substitutable for T_g . These estimations are supported from ΔT_x , ΔT_{cross} and specific temperatures summa-

Fig. 5 Plots of (a) x , (b) dx/dT and the approximate solution (x_{ap}) calculated by eq. (15) for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ metallic glass. (c) the details of the changes in the x and x_{ap} near T_g .

Table 2 Calculated temperatures for Ni, metallic glasses and SiO₂ systems. The T_g^{Exp} is the glass transition temperature experimentally determined, and refers to previous data.⁴⁾ The ΔT_{cross} is defined as $\Delta T_{\text{cross}} = T_x - T_{\text{cross}}$ where $T_{\text{trans.f}} = T_x$.

Alloy	$T_{\text{trans.s}}/\text{K}$	$T_{\text{cross}}/\text{K}$	$T_g^{\text{Exp}}/\text{K}$	T_g/K	T_x/K	$\Delta T_x/\text{K}$	ΔT_{cross}
Ni	458	480	425	500.3	520.4	20.1	40.4
Fe ₈₃ B ₁₇	740	756	760	766.3	773.0	6.7	17.0
Co ₇₅ Si ₁₅ B ₁₀	765	775	785	789.1	792.5	3.4	17.5
Fe ₇₉ Si ₁₀ B ₁₁	797	810	818	820.6	826.0	5.4	16.0
Fe ₈₀ P ₁₃ C ₇	718	733	736	745.6	752.9	7.3	19.9
Ni ₇₅ Si ₈ B ₁₇	762	775	782	786.4	791.8	5.4	16.8
Pt ₆₀ Ni ₁₅ P ₂₅	512	528	500	543.2	555.9	12.7	27.9
Pd ₈₂ Si ₁₈	646	659	657	671.9	677.9	6.0	18.9
Ni _{62.4} Nb _{37.6}	916	930	945	941.2	946.6	5.4	16.6
Pd _{77.5} Cu ₆ Si _{16.5}	645	659	653	671.2	677.2	6.0	18.2
Pd ₄₀ Ni ₄₀ P ₂₀	601	615	602	627.6	634.3	6.7	19.3
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	560	578	581	591.5	602.2	10.7	24.2
Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5}	603	629	602	645.1	664.5	19.4	35.5
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	592	620	595	637.7	660.5	22.8	40.5
Nd ₁₃ Fe ₇₉ B ₈	659	678	—	694.0	708.7	14.7	30.7
Nd ₁₆ Fe ₇₆ B ₈	652	683	—	703.3	734.8	31.5	51.8
Mg ₆₅ Cu ₂₅ Y ₁₀	454	486	413	505.7	527.1	21.4	41.1
Mg ₆₅ Ni ₂₀ Nd ₁₅	411	431	459.3	446.1	452.8	6.7	21.8
Mg ₆₅ Ni ₂₀ Nd ₁₅	665	713	459.3	736.2	785.8	49.6	72.8
SiO ₂	1175	1230	1495	1244.0	1299.6	55.6	69.6

rized in Table 2. It is thus found that one can estimate T_g and ΔT_x with the approximate solution of eq. (7) from the $x - T$ diagram. This leads to an important result that one does not have to analyze the differential equation numerically in order to calculate the ΔT_x .

It is also to be noted in Fig. 5(c) that ΔT_{trans} has a relationship with the acute angle between x_{eq} and x_{lin} at T_{cross} ;

$$\Delta T_{\text{trans}} \propto \left. \frac{d(x_{\text{eq}} - x_{\text{lin}})}{dT} \right|_{T=T_{\text{trans}}} \quad (16)$$

Since x_{lin} is fixed in the present study, ΔT_{trans} depends on the value of dx_{eq}/dT ($= 1/B$). This is supported by the results in Fig. 3 that ΔT_x is in proportion to B . Thus, the $x - T$ diagram is useful for estimating T_g as well as ΔT_x .

Figure 6 shows the $x - T$ diagram in which x_{ap} and x_{eq} for the systems listed in Table 1 are plotted. From this figure, one can estimate T_g for each system as the T_{cross} between x_{lin} and x_{eq} by the above-described method. Furthermore, ΔT_x can be estimated by eq. (16). These results support the contention that the largest ΔT_x can be calculated for the SiO₂ system having low T_0 as well as the largest B .

4.2 The reason for the discrepancy between the calculated and experimental ΔT_x

As shown in Fig. 4, the calculated values of ΔT_x were approximately six times smaller than the experimental results. We will discuss the reason for this discrepancy on the basis of the definition of T_g and T_x .

Figure 7 shows the plots of the calculated and experimental T_g for the systems listed in Table 1. The x - and y -axis show the experimentally obtained (T_g^{e}) and the calculated (T_g^{c}), respectively. From Fig. 7, the plots of the T_g -values roughly lie along the broken line except for the SiO₂ system, indicating the directly proportional relationship between the T_g -values.

Fig. 6 Free volume-temperature ($x - T$) diagram in which the x_{ap} and x_{eq} for Ni, metallic glasses and SiO₂ systems are plotted.

This result implies that T_g is correctly calculated in the present model using the given C_0 and E_f values. It is thus suggested that the discrepancy in ΔT_x results in the definition of T_x .

As described in Section 2, T_x is defined as the temperature where x is exactly equal to x_{eq} . This definition of T_x is apparently a necessary condition; hence, other factors described below also affect T_x .

The first factor is the relaxation due to the short-range order. As far as the relaxation is concerned, it has been pointed out¹⁸⁾ that there are two types of relaxation: the topological short range order (TSRO) and the chemical short range order (CSRO). The former is due to the change in free volume: this is the form of relaxation which the present model deals

Fig. 7 Plots of the calculated and experimental T_g values for Ni, metallic glasses and SiO_2 systems.

with. By contrast, the CSRO cannot be taken into account for the present calculation model. Although the effect of CSRO on crystallization has not been clarified, the change in atomic configurations due to the CSRO causes an increase in T_x .

The second factor is probably due to the difficulty of atomic rearrangements which stabilize the supercooled liquid and prevent crystallization.²⁾ For instance, it has been experimentally confirmed in thermal analysis that crystallization from the stabilized supercooled liquid occurs through simultaneous precipitation of more than two phases.²⁾ It has also been shown experimentally in a Zr–Al–Cu system that the appearance of the extremely large supercooled liquid range is attributable to retardation of growth of the $\text{Zr}_2(\text{Cu}, \text{Al})$ phase.²⁾ This requires the long-range diffusion of Al to redistribute Al around Zr even in a highly dense random packed structure. Thus, the second factor is due to the difficulty in the precipitation of the crystalline phase from a stabilized supercooled liquid, a factor which cannot be taken into account in the present calculation model.

In addition to the above factors, E_f and C_0 can be factors affecting ΔT_x . First, we will discuss the validity of the calculation condition that E_f and C_0 are constants, which implies that they are independent in alloy systems. The values of $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$ ¹⁸⁾ used in the present study were originally obtained for the Pd-based metallic glasses from the kinetics of free volume annihilation which were obtained from experiments on the isothermal changes in viscosity, resistivity, elastic constants *etc.*^{25–27)} The other sets of values used for the analysis of glass transition phenomena are exemplified as $(E_f, C_0) = (99 \text{ kJ/mol}^{-1}, 8.4 \times 10^{15} \text{ s}^{-1})$ for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass,²²⁾ and $(E_f, C_0) = (250 \text{ kJ/mol}^{-1}, 1.63 \times 10^{25} \text{ s}^{-1})$ for $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ metallic glass.²⁸⁾ In order to estimate errors in ΔT_x with the values of E_f and C_0 , calculations were carried out for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ and $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ metallic glasses as shown in Fig. 8. In the calculation, B and T_0 of the $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ ⁴⁾ were used instead of those of $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ alloy because of the close similarity

Fig. 8 The changes of dx/dT profiles of $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ calculated with (E_f, C_0) for both their intrinsic values and the present calculation conditions.

in the compositions. From the dx/dT profiles in Fig. 8, the $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ metallic glass shows ΔT_x of 18 K for $(E_f, C_0) = (99 \text{ kJ/mol}, 1.63 \times 10^{25} \text{ s}^{-1})$, and 10 K for $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$. On the other hand, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass shows ΔT_x of 30 K for $(E_f, C_0) = (250 \text{ kJ/mol}, 8.4 \times 10^{15} \text{ s}^{-1})$, and 20 K for $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$. Thus, the difference in ΔT_x is 8 K for $\text{Fe}_{41.5}\text{Ni}_{41.5}\text{B}_{17.5}$ and is 10 K for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ metallic glass. Accordingly the ratio between the ΔT_x calculated with $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$ and with the intrinsic values are estimated as approximately 50%. Thus, it is shown that no significant differences in ΔT_x are seen in the calculation results although the calculations were carried out under the condition that $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$ instead of the intrinsic values of E_f and C_0 . This result enabled us to use $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$ for other alloys systems except Pd-based metallic glasses.

Furthermore, hypothetical calculations were carried out for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy in order to clarify the influence of E_f and C_0 on the value of ΔT_x . Figure 9 shows the contour lines of ΔT_x , in $E_f - C_0$ diagram under the calculation condition that $B = 8444 \text{ K}$ and $T_0 = 372 \text{ K}$, and the representative dx/dT profiles. Because no values of E_f and C_0 are given for the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy, we assume that this alloy has $(E_f, C_0) = (160 \text{ kJ/mol}^{-1}, 2.1 \times 10^{23} \text{ s}^{-1})$. In Fig. 9(a), ΔT_x was calculated as 11 K in the sets of (E_f, C_0) values on the line abc, as 22 K on the line def, and as 44 K in on the line ghi. Since the calculations were conducted using the condition that $(E_f, C_0) = (160 \text{ kJ/mol}^{-1}, 2.1 \times 10^{23} \text{ s}^{-1})$ for all the alloys in the present study, the calculation results have errors resulting from the fact that we did not use the intrinsic values of E_f and C_0 . The values for ΔT_x were overestimated by a factor of nearly two in the alloys having (E_f, C_0) plotted in the area between lines abc and def. In contrast, the alloys having (E_f, C_0) plotted in the area between lines ghi and def were underestimated to the same degree. However, in the present study, ΔT_x was calculated in a range from approximately 5 K more than 20 K, as shown in Fig. 4(b). This result indicates that the values of ΔT_x were affected more significantly by the values of (B, T_0) than by those of (E_f, C_0) .

Thus, the results shown in Figs. 8 and 9 support the

Fig. 9 (a) The contour lines of ΔT_x in the E_f - C_0 diagram calculated with the values $B = 8444$ K and $T_0 = 372$ K. Experimental values of E_f and C_0 ^{18,22,28} are also shown by open circles. "No relaxation" indicates that no decrease in x as well as dx/dT was calculated before glass transition. (b) dx/dT profiles calculated with the E_f and C_0 denoted in Fig. 9(a).

present calculation condition that E_f and C_0 can be fixed as $(E_f, C_0) = (160 \text{ kJ/mol}, 2.1 \times 10^{23} \text{ s}^{-1})$.

Thus, the simultaneous lack of the two factors in the present calculation model is presumed to affect the discrepancy between the calculated and experimental ΔT_x values.

4.3 The relations between the VFT parameters and R_c , T_g/T_m or ΔT_x

We discuss here the validity of the present calculation model using the VFT parameters for viscosity. In our previous paper, we succeeded in obtaining the theoretical relation corresponding to R_c and T_g/T_m ¹⁷⁾ from the time-transformation diagram. In this study, the time-transformation diagram was calculated using the VFT parameters and T_m as the minimal necessary parameters. The subsequent analysis was made to clarify the relationship between R_c and ΔT_x using the VFT parameters. It is significant that the relationship among the GFA factors have been obtained from the VFT equation for viscosity. Figure 10 shows the relationship between the VFT parameters and the GFA factors. It is seen that the viscosity is a key factor to derive all the GFA parameters (R_c , T_g/T_m and ΔT_x). From the figure, the minimum necessary parameters for R_c and T_g/T_m are all the VFT parameters (η_0 , B and T_0) and melting temperature (T_m) whereas that for ΔT_x is B and T_0 . Figure 10 also shows that the GFA parameters and their relations can be derived from the VFT parameters for viscosity. To the best of our knowledge, these relations are firstly

Fig. 10 The relation between the VFT parameters and the GFA factors.

derived from within the framework of this unique model. The viscosity term used in our previous study¹⁷⁾ and the present studies is mathematically independent of other terms for the calculation, and hence the other viscosity models can be substitutable for the VFT expression.

5. Conclusions

The conclusions derived from the present results and discussion are summarized as follows.

- (1) The maximum value of ΔT_x was calculated as 56 K for the SiO_2 system. The $\log R_c$ tends to decrease linearly with increasing ΔT_x . This tendency is consistent with the experimental result.
- (2) The calculated ΔT_x values for some metallic glasses are approximately six times smaller than the experimental results. The discrepancy between the calculated and experimental ΔT_x values is due to the lack of the effects of the chemical short range order and the difficulty in the diffusivity for crystallization in the present calculation model.
- (3) From the approximate solution of the differential equation, it was clarified that the T_g and ΔT_x can be derived by the schematic-analysis method in the $x - T$ diagram.
- (4) It is recognized that viscosity is the key factor which affects all the GFA parameters (R_c , T_g/T_m and ΔT_x). It was also clarified that the minimum necessary parameters for the calculation of each GFA parameter are all the VFT parameters (η_0 , B and T_0) and melting temperature (T_m) for R_c and T_g/T_m , and B and T_0 for ΔT_x . It has been shown that the GFA parameters and their relations can be derived from the VFT parameters for viscosity.

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