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Direct Comparison between Critical Cooling Rate and Some Quantitative Parameters for Evaluation of Glass-Forming Ability in Pd–Cu–Ni–P Alloys

Nobuyuki Nishiyama[1] and Akihisa Inoue[1,2]

[1]*Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation, Sendai 982-0807, Japan*
[2]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

The quantitative parameters such as supercooled liquid region or several reduced glass transition temperatures were applied for evaluating the glass-forming ability of Pd-based metallic glasses. A distinct proportional tendency was recognized between measured critical cooling rates and reduced glass transition temperature by liquidus temperature rather than eutectic temperature. Significance and physical meanings of the quantitative parameters for evaluating of glass-forming ability were also discussed. Furthermore, a new concept of a modified reduced glass transition temperature was proposed to evaluate the glass-forming ability. The modified reduced glass transition temperature as a function of critical cooling rate was found to exhibit a much clear linearity.

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1. Introduction

For the last decade, multi-component alloy systems with particular compositions have been reported to cause a significant increase in glass-forming ability (GFA). As a result, bulk metallic glasses (BMG) with a diameter of 72 mm were prepared. Great efforts have been devoted to evaluate the GFA in the multi-component systems. Some parameters such as temperature interval of supercooled liquid region (ΔT_x; defined as on-set of crystallization temperature (T_x)-glass transition temperature (T_g) or reduced glass transition temperature (T_{rg}; defined as the ratio of T_g to melting temperature (T_m)) have been used for evaluating GFA of metallic glasses. However, the importance of T_{rg} was already suggested in early 1930's. In the beginning of the research for non-crystalline materials, Tanmann had first pointed out the importance of T_{rg} using his empirical fact.[1)] After then, Kauzamann[2)] has introduced his "two-third rules", *i.e.*, T_g can be expressed as approximately two third of T_m. The rule was confirmed in several symmetrical and unsymmetrical structured polymer systems.[3–5)] At that time, Turnbull applied the Classical Nucleation Theory (CNT) to some inorganic materials for evaluating the GFA and successfully underlined its overall features.[6)] He also pointed out the significance of the T_{rg}. Since these efforts, T_{rg} has been used for evaluating GFA even at present. On the other hand, temperature interval of supercooled liquid region (ΔT_x; defined as on-set of crystallization temperature (T_x) $-$ T_g) was used for evaluating GFA. This parameter was first introduced by Inoue.[7)] Focusing on this parameter, it is the fact that a number of new metallic glasses such as Ln-,[8,9)] Mg-,[10,11)] Zr-,[12,13)] Fe-[14,15)] and Co-[16)] have been found by Inoue's group. However, little is known about direct relation between measured critical cooling rate for glass formation (R_c) and the above-mentioned parameters. The usefulness of these parameters has not been fully understood yet.

We have already reported that a $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy has an extremely high GFA and a low critical cooling rate for glass formation (R_c) of 0.10 K/s.[17–20)] This exceptional high thermal stability and retarded crystallization kinetics enable us to investigate the nature of the undercooled melt, *i.e.*, thermodynamics,[21)] viscosity,[22)] thermal expansion,[23)] elastic modulus[24)] and other properties. It is most important to note that the present authors have first measured the R_c under continuous cooling for the alloy and completed Continuous-Cooling-Transformation (CCT) diagram among the metallic glasses. When we use the Pd–Cu–Ni–P alloys with intentionally modified compositions, it would be possible to clarify the relationship between the measured R_c and these quantitative parameters. This paper intends to clarify the usefulness of these parameters for evaluating GFA of Pd–Cu–Ni–P alloys as a typical metallic glass. Furthermore, the physical meaning of each parameter in the aspect of GFA is discussed.

2. Experimental Procedure

A Pd–P pre-alloy was prepared using a high purity of phosphorus polycrystal (up to 99.9999% purity). Then, 14 kinds of quaternary Pd–Cu–Ni–P master ingots with different compositions were prepared by arc melting the mixtures of pure-Pd, -Ni, -Cu and pre-alloyed Pd–P in an Ar atmosphere. Using prepared ingots, fully vitrified ribbon samples with a width of about 0.02 and a thickness of about 1 mm were obtained by a single-roller melt-spinning technique. Glassy natures of the ribbon samples were examined by X-ray diffactmetry (XRD). To clarify the thermal characteristic temperature, differential scanning calorimeter (DSC) measurement was carried out using a power-compensated DSC with an absolute temperature accuracy better than ± 0.1 K. Graphite pan was used and measured at a heating rate of 0.67 K/s up to 998 K. In constructing Continuous-Cooling-Transformation (CCT) diagrams and evaluating R_c, a high-vacuum high-temperature DSC was used with a highly purified Ar atmosphere (less than 10-ppm oxygen content). Temperature deviation of the equipment from the cooling program was evaluated within ± 2.0 K. Each sample was weighed within 10 ± 0.5 mg and embedded into an Al_2O_3 pan. Prior to the cooling measurement, the B_2O_3 flux treatment[25)] was repeatedly (typically 10

times) made to eliminate heterogeneous nucleation. The samples together with the flux medium were initially heated up to 1073 K and kept at this temperature for 600 s to ensure complete melting. Then the molten samples were cooled at different cooling rates ranging from 0.150 to 0.017 K/s for constructing a CCT diagram. The cross sectional structure of the samples cooled in the HV/HT-DSC was examined with an optical microscope (OM) using a polarized observation method in order to determine accurate R_c.

3. Results

Glassy natures of all the ribbon samples were confirmed by XRD (not shown here). For example, heating DSC traces of the glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ and $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ ribbon samples are shown in Fig. 1. Both of the traces show typical curves, *i.e.*, an endothermic reaction due to glass transition, followed by a rather large supercooled liquid region and then a sharp exothermic reaction due to crystallization. T_g, T_x, eutectic temperature (T_e) and liquidus temperature (T_l) are determined as denoted in the figure. Based on these characteristic temperatures, quantitative parameters are obtained. Figure 2 shows continuous cooling curves of the molten $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ alloy obtained at cooling rates ranging from 0.100 to 0.017 K/s. No recalescence is seen on the cooling curves obtained at the rates above 0.067 K/s. In addition, a curvature bending due to glass transition at 580 K is also seen in the curves without recalescence. However, a clear recalescence phenomenon due to precipitation of crystalline phases can be seen in the curves at the cooling rates below 0.050 K/s. Therefore, the R_c for the $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ melt is assumed to be as low as 0.067 K/s. In order to determine an accurate R_c, cross sectional structure was examined by polarized OM. Figure 3 shows the cross sectional micrographs for the $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ melt obtained by cooling of the same samples. As seen in the micrograph of the sample cooled at the rate of 0.050 K/s, a large crystalline grain with a small amount of surface crystallization can be observed. However, no contrast of a crystalline phase is seen in the samples cooled at the rate above 0.067 K/s. Therefore, it is concluded that the R_c for the $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ melt is 0.067 K/s. During the same process, the R_c for the 14 samples were determined. Table 1 summarizes the alloy compositions for the 14 samples (No. 0 to 13) used in the present study, characteristic temperatures, calculated quantitative parameters and measured R_c. One can notice that the T_g and T_x are varied with their compositions, though all the samples exhibit nearly the same T_e ($= 800 \pm 5$ K). It is assumed that the samples have different crystallization kinetics, though all the samples have nearly the same eutectic melting. This assumption would be supported from measured R_c. The measured R_c of the samples are also varied from 0.067 K/s to over 0.150 K/s, depending on compositions. Figure 4 plots the three parameters ((a) ΔT_x, (b) T_g/T_e and (c) T_g/T_l) as a function of R_c. Approximate linear lines by the least square method are seen. Only the relation of the T_g/T_e value shows negative cooling rate dependence, indicating that the T_g/T_e is not a dominant parameter for the GFA. On the other hand, the other two parameters exhibit a positive dependence. The alloy with the maximum value of ΔT_x ($= 87$ K for the No. 0 sample) does not correspond to the alloy with the minimum value of R_c ($= 0.067$ K/s for the No. 7 sample). It is therefore concluded that the value of ΔT_x would be difficult to be applied for evaluating quantitatively GFA. The values of T_g/T_l can rather well describe the tendency of GFA, though the plots are slightly fluctuated. Lu *et al.* have already predicted the importance of $T_g T_l$ using calculated R_c for the typical La-, Mg- and Pd-based metallic glasses.[26] They didn't discuss the usefulness of the parameter for detailed variation in alloy composition, though they discussed optimum compositions for glass formation. Although the results obtained are almost consistent with their assumption, the importance of the present results is attributed to the accurate data on R_c. Consequently, the GFA for the alloys can be represented much accurately by the parameter of $T_g T_l$. In other words, the alloy

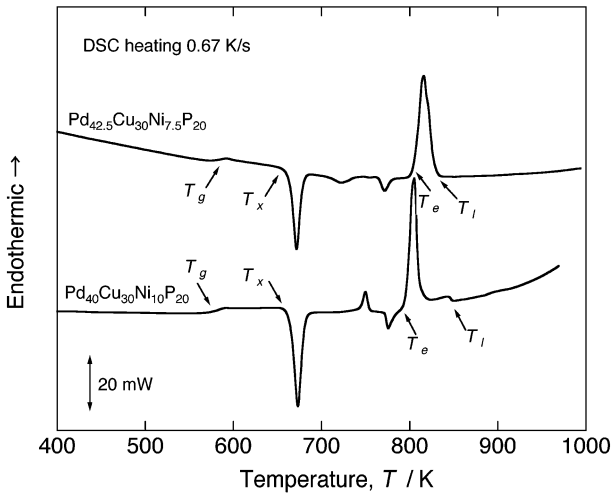

Fig. 1 DSC traces of glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ and $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ ribbons obtained by isochronal heating at a heating rate of 0.67 K/s.

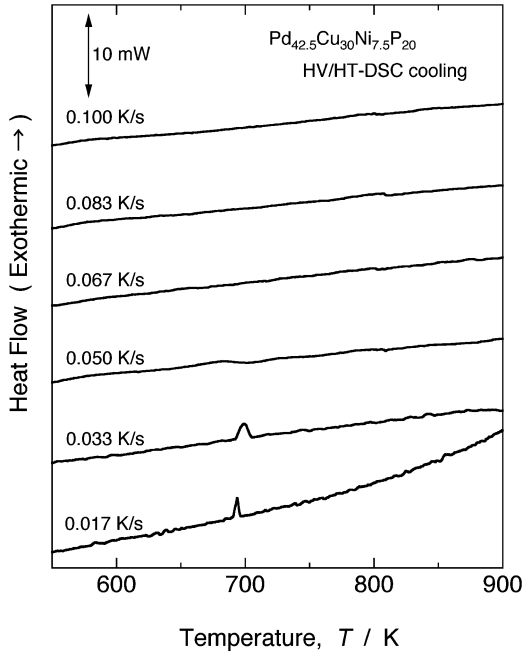

Fig. 2 Heat flow curves of a $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ melt with a weight of about 10 mg which were cooled at various rates between 0.100 to 0.017 K/s in the embedded state with B_2O_3 flux medium.

Table 1 Thermal characteristic temperatures, quantitative parameters for estimation of glass-forming ability and measured R_c for a series of glassy Pd–Cu–Ni–P alloys with different compositions and the same eutectic melting.

No.	Composition (at%)	T_g (K)	T_x (K)	ΔT_x (K)	T_e (K)	T_l (K)	T_g/T_e	T_g/T_l	R_c (K/s)
0	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	570	657	87	795	848	0.717	0.672	0.100
1	$Pd_{40}Cu_{32.5}Ni_{7.5}P_{20}$	568	654	86	799	932	0.711	0.609	0.133
2	$Pd_{40}Cu_{35}Ni_{5}P_{20}$	556	636	80	800	857	0.696	0.649	>0.150
3	$Pd_{40}Cu_{27.5}Ni_{12.5}P_{20}$	583	665	82	801	897	0.728	0.649	>0.150
4	$Pd_{40}Cu_{25}Ni_{15}P_{20}$	596	668	72	803	910	0.742	0.654	0.150
5	$Pd_{42.5}Cu_{27.5}Ni_{10}P_{20}$	584	665	81	804	871	0.727	0.671	0.083
6	$Pd_{45}Cu_{25}Ni_{10}P_{20}$	595	675	80	805	884	0.739	0.673	0.100
7	$Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$	576	658	82	803	834	0.718	0.691	0.067
8	$Pd_{45}Cu_{30}Ni_{5}P_{20}$	577	659	82	804	861	0.718	0.670	0.083
9	$Pd_{37.5}Cu_{32.5}Ni_{10}P_{20}$	572	647	75	800	929	0.715	0.615	0.013
10	$Pd_{35}Cu_{35}Ni_{10}P_{20}$	564	641	77	801	876	0.704	0.643	>0.150
11	$Pd_{37.5}Cu_{30}Ni_{12.5}P_{20}$	573	658	85	801	905	0.715	0.633	>0.150
12	$Pd_{35}Cu_{30}Ni_{15}P_{20}$	577	659	82	798	947	0.723	0.609	>0.150
13	$Pd_{45}Cu_{27.5}Ni_{7.5}P_{20}$	592	662	70	805	890	0.735	0.665	>0.150

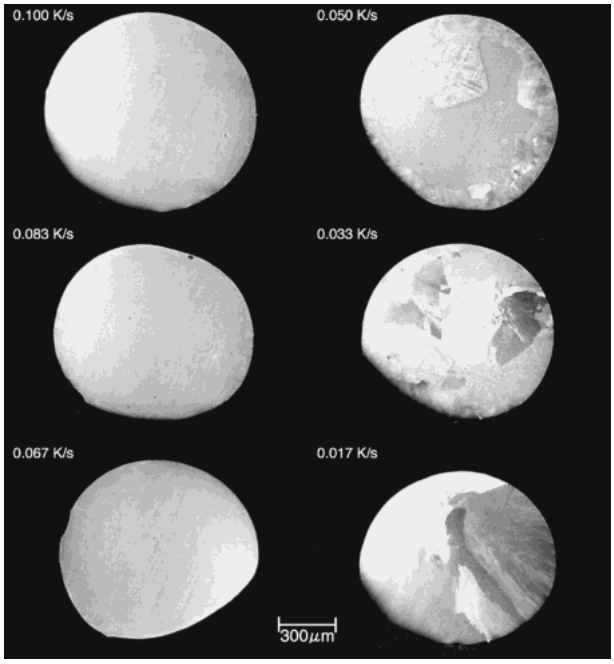

Fig. 3 Cross sectional optical micrographs of $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ alloys prepared at cooling rates from 0.100 to 0.017 K/s.

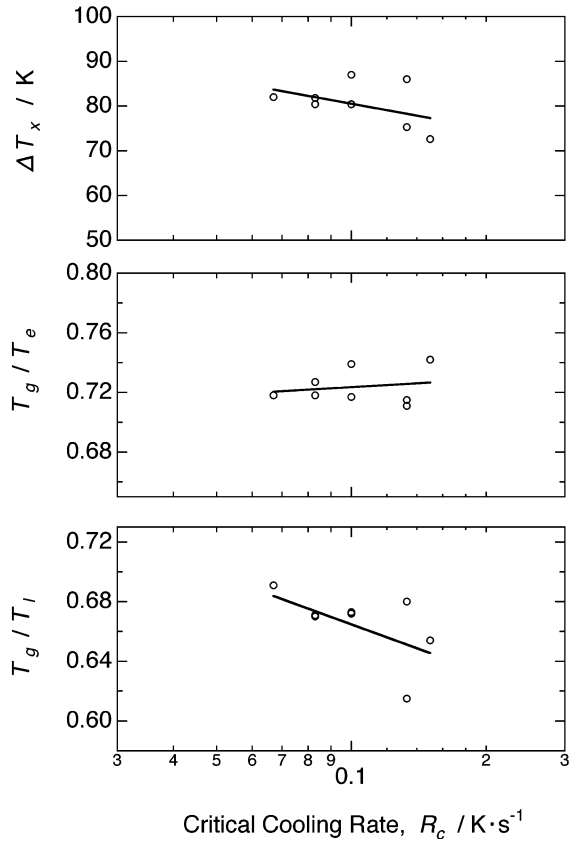

Fig. 4 Relationship between the quantitative parameters (ΔT_x (a), T_g/T_e (b) and T_g/T_l (c)) and measured R_c for Pd–Cu–Ni–P glassy alloys.

with just eutectic composition can be more easily vitrified in the multi-component metallic glasses. In the next section we will discuss the significance of these parameters. In addition, we intend to introduce a modified parameter which is taken the compositional effect into consideration.

4. Discussion

The significance of the quantitative parameters for evaluating GFA will be discussed with the aim of clarifying their physical meaning. The parameter ΔT_x, so called "supercooled liquid region", is defined as the temperature interval between T_x and T_g. T_x contains crystallization kinetics. T_g contains purely thermodynamic meaning to avoid the Kauzmann Paradox.[2)] Therefore the parameter can be recognized as a stable region of undercooled liquid from the glass-to-supercooled liquid transition temperature till the temperature where the volume fraction of crystal exponential increasing. The parameter can well contain both thermodynamics and crystallization kinetics of primary precipitation, but the parameter represents the resistance against crystallization only in the temperature range near T_g. Even in the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy with exceptionally high thermal stability, T_x is almost the same as its nose temperature (T_n) in the CCT diagram. In almost all the metallic glasses with less thermal stability than $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy, the value of T_x

should be lower than T_n. Consequently, ΔT_x will show the crystallization kinetics even only the temperature range between T_g and T_n. In general, GFA of the alloy is determined in the temperature range between T_m and T_n. Hence GFA of the alloy cannot be discussed by the magnitude of ΔT_x. The parameter of ΔT_x should be better to use only for evaluating the thermal stability of supercooled liquid.

The reduced glass transition temperature, so-called "T_g/T_m", contains some kinetics factors. Once fixed the values of T_g, T_m, the time passing through the undercooled liquid region ($T_m - T_g$) can be determined at certain cooling rate. However, uncertainty in this parameter is that the devitrification kinetics is not considered. In addition, the parameter should be rigorously applied only for simple liquid systems because T_m can be uniquely defined only in a simple liquid system. Extensively speaking, the parameter may be applied for evaluation of GFA for just eutectic system and/or the glass-forming systems which showing polymorphous crystallization. For this reason, it is assumed that the values of T_g/T_e are inconsistent with measured R_c in the present study, and concluded that the parameter of T_g/T_e cannot completely represent the GFA of off-eutectic systems. On the other hand, the values of T_g/T_l are relatively consistent with the measured R_c. The parameter of T_g/T_l is taken over the whole temperature range between T_g and T_l where the undercooled liquid can exist. The reason for the slight fluctuation in plots in the Fig. 4(c) is because the parameter of T_g/T_l did not contain the structural factor of primary precipitation. In other words, the incompleteness of the parameter is the fact, *i.e.*, T_l in the parameter of T_g/T_l is dealt as a melting temperature, which is defined uniquely in the simple liquid. However, all the alloys except for No. 7 show off eutectic melting. It is therefore required to modify the parameter in order to evaluate GFA even in the multi component systems with off eutectic composition.

Here, we intend to introduce a modified parameter, which is taken the compositional effect into consideration. As seen in the DSC trace of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ in Fig. 1, one can see the large endothermic peak due to eutectic melting and the small peak due to liquidus melting. How far from the eutectic point for the alloy with a certain composition can be represented as the ratio of T_e to T_l. The ratio should be normalized by lower limit of existing undercooled liquid, *i.e.*, T_g. Therefore, an appropriate modified coefficient (α), which takes the values between 1 and 0, is defined as

$$\alpha = (T_e - T_g)/(T_l - T_g) \quad (1)$$

By using the coefficient, the modified parameter can be represented as a multiple of T_g/T_l and α. If T_l is equal to T_e (equilibrium eutectic melting or melting of simple liquid), the value of α comes to 1, and there is no effect for the value of T_g/T_l. In the multi component system with eutectic composition, T_l is slightly higher than T_e, because the melting occurs as a first order of transformation at a certain heating rate. The value of α in the multi component metallic glass with eutectic composition will lie below 1 and hence enlarge the difference as compared with T_g/T_l. This wide range expression is expected to lead to an accurate evaluation of GFA. Furthermore, the most important meaning of introducing α is to add the compositional effect to the parameter of T_g/T_l. In general, T_l increases with an increase in the compositional deviation from eutectic point. That is, the value of the modified T_g/T_l will decrease with increasing the compositional deviation from eutectic point. Figure 5 shows the relationship between the modified T_g/T_l and measured R_c. The modified T_g/T_l can represent the measured R_c well, and a clear linearity can be seen in the relation, indicating that the modified T_g/T_l is applicable in the evaluation of GFA even for metallic glasses with a composition of off eutectic. The detailed equilibrium phases and primary phase identification will be reported in the near future. The information is expected to increase an accuracy of evaluation.

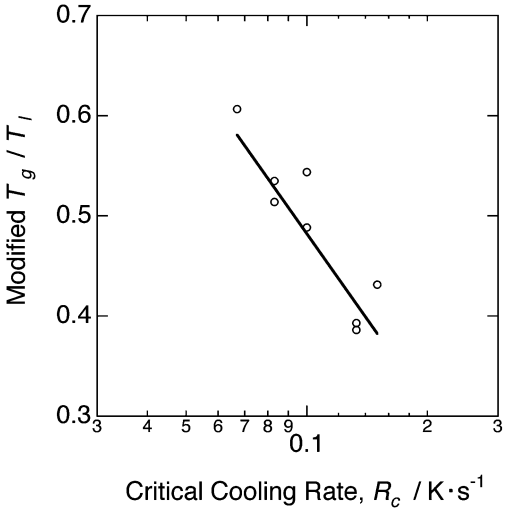

Fig. 5 Relationship between the modified parameters ($\alpha T_g/T_l$) and measured R_c for Pd–Cu–Ni–P glassy alloys.

5. Conclusions

The relationship between measured R_c and quantitative parameters such as ΔT_x, T_g/T_e and T_g/T_l were examined for the series of Pd–Cu–Ni–P alloys with different compositions and the same eutectic melting. The T_g/T_l showed a better correlation to the measured R_c rather than the other two parameters, though the plot as a function of R_c was fluctuated. The fluctuation indicates that the parameter of T_g/T_l still contains incompleteness. The reason for the incompleteness was assumed that the parameter did not take the structural factor of primary precipitation into consideration. With the aim of evaluating more accurately GFA for off-eutectic alloys, we introduced the modified T_g/T_l, which can be regarded as the compositional effect parameter far from the eutectic point. As a result, the modified T_g/T_l exhibited a much better linearity against the measured R_c. It is therefore expected that the concept of modified parameter is applied even for other multi component metallic glasses with compositions of off eutectic.

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