# Estimation of Glass Forming Ability of Amorphous Alloys Based on the Thermal Analysis Data during Cooling

Sang-Bok Lee[1,*], Sang-Kwan Lee[1] and Nack J. Kim[2]

[1]*Korea Institute of Machinery and Materials, Changwon 641-010, Korea*
[2]*Center for Advanced Aerospace Materials, Pohang University of Science and Technology, Pohang, 790-784, Korea*

Based on the analytic approach, a new parameter $\Delta T_m$ (reduced difference of nucleation temperatures) for estimating the glass forming ability (GFA) has been suggested with simple DTA data at two different cooling rates. The new parameter described GFA of amorphous alloys very well. Besides, an equation for estimating the critical cooling rate has also been suggested using the new parameter for GFA. The results of prediction model have been in good agreement with the previous experimental results.   [doi:10.2320/matertrans.MRA2007026]

## 1. Introduction

Recently, there have been growing interests in bulk amorphous materials due to their unique properties such as high strength, elastic limit of about 2%, excellent wear resistance, and high corrosion resistance. In these material systems, an understanding of the glass forming ability (GFA) is essential to clarify the formation mechanisms of amorphous/crystalline phases, which provides better design of new bulk amorphous alloy systems as well as ultra-fine microstructures.

Based on the heterogeneous nucleation theory and thermal analysis data, an approach to the understanding of the crystallization kinetics of bulk amorphous alloys has been developed in our previous study. It successfully described the crystallization behavior of the well-known $Zr_{41.2}Ti_{13.8}$-$Cu_{12.5}Ni_{10}Be_{22.5}$ alloy.[1–3] However, in the general amorphous alloy systems, except for Zr-Ti-Cu-Ni-Be and Pd-Cu-Ni-P alloys, there are very limited information on thermophysical properties such as the viscosity, the interface energy between liquid and crystalline phases, and the heat of fusion. These factors make it ambiguous to describe the crystallization kinetics of bulk amorphous alloys. For this reason, many studies have been carried to determine the parameter for the estimation of GFA without previous knowledge of thermophysical properties. The key parameter among many descriptions for GFA is the critical cooling rate $R_c$, which is utilized in designing new bulk amorphous alloys.[4,5] Since $R_c$ is very difficult to measure, there have been great efforts in searching for a reliable parameter and a simple method to quantify $R_c$ for amorphous alloys. Several indicators have been used to describe GFA or $R_c$. Among these parameters, the reduced glass transition temperature $T_{rg}$ $(= T_g/T_l)$ and the supercooled liquid region $\Delta T_x$ $(= T_x - T_g)$ have been mostly used. Although a new parameter $\gamma$ $(= T_x/(T_g + T_l))$ was suggested by Lu and Liu[6] recently, the parameters $T_{rg}$, $\Delta T_x$ and $\gamma$ have shown contrasting trends with GFA in some alloy systems.[6–9]

The critical cooling rate $R_c$ of amorphous alloy has been evaluated by several methods. $R_c$ has been calculated by

Uhlmann and Davies' approach based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model of crystallization.[10,11] Using thermal analysis (DSC/DTA) data, Barandiaran and Colmenero proposed a method which was analyzed by a formula based on the non-isothermal crystallization kinetics.[12,13] Despite the numerous studies on new indicators for GFA and formulation for $R_c$, universal parameter and formula have not been developed. Therefore, further investigation is necessary to obtain a more precise parameter and to develop better quantification methods to describe the GFA of amorphous alloys.

In this study, based on analytic results of various alloys ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Mg_{65}Cu_{25}Gd_{10}$, $Mg_{65}Cu_{25}Y_{10}$, and $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$), a new parameter for GFA has been suggested. An estimation equation of critical cooling rate, representing parameters of the glass formation in amorphous alloys, has also been proposed. The model predictions have been compared with both the previous experimental results and the calculated results from the approach of crystallization kinetics on cooling.

## 2. Crystallization Behavior of Amorphous Alloy

In the previous study, we proposed that the crystallization of amorphous alloys was originated from the heterogeneous nucleation process with catalyses in the continuously cooled liquid.[1,2] Based on the heterogeneous nucleation theory and the thermal analysis data, a method of calculating the critical cooling rate $R_c$, TTT diagram, and CCT diagram was proposed.

The powders produced by uniform droplet spray (UDS) process[14] were subjected to thermal analysis (DTA) in order to investigate the crystallization behavior of amorphous alloys. Figure 1 shows the DTA traces of the $Zr_{41.2}Ti_{13.8}$-$Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at two different cooling rates ($R = 5$ K/min and 20 K/min). The black arrows indicate the nucleation temperatures (onset crystallization temperature) $T_n$. It can be seen that $T_n$ shifts to a lower temperature with the increase of cooling rate. The liquidus temperature $T_l$ of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was also analyzed by DTA.

Using the kinetic approach,[2,14] the onset crystallization

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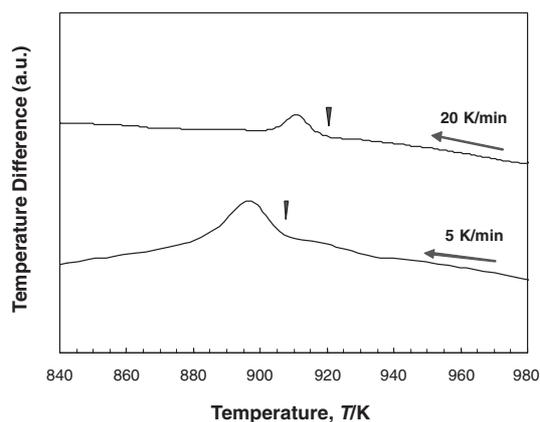*Corresponding author, E-mail: leesb@kmail.kimm.re.kr

Fig. 1 DTA traces at cooling rates of 5 K/s and 20 K/min for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy on continuous cooling.[2]
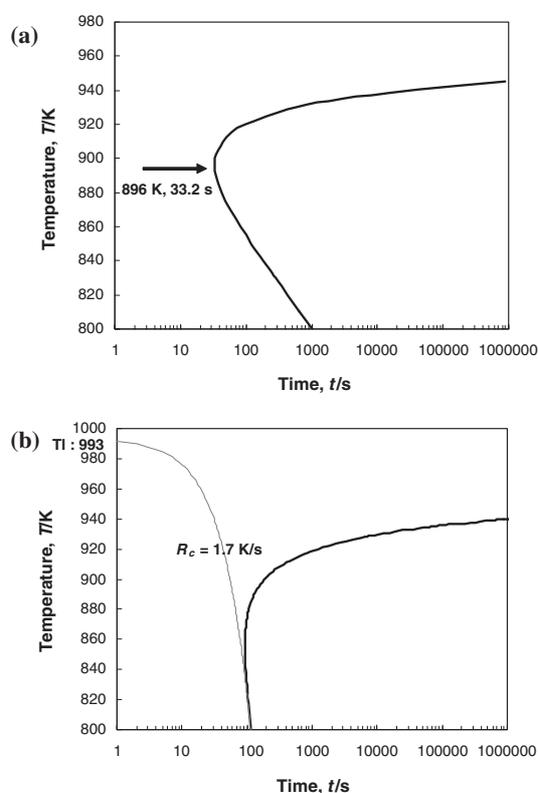


Fig. 2 The onset of crystallization of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy as a function of undercooling: (a) calculated time temperature transformation (TTT); (b) calculated continuous cooling transformation (CCT) diagram.[2]

behavior of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was analyzed without special regards to the phase formation sequence at different temperatures. The parameters used for analyzing crystallization kinetics are described in reference.[1] Figure 2 illustrates the calculated TTT and CCT diagrams using our approach, which were constructed by gathering the data of nucleation temperatures and times at various isothermal temperatures and cooling rates. The nose time $t_c$ and the nose temperature $T_c$ in the TTT diagram were calculated to be 33.2 s and 896 K, respectively. These results are in good agreement with the experimental results of

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy,[15] which showed the nose time of 60 s and the nose temperature of 895 K. The critical cooling rate was calculated to be 1.7 K/s, which was also in good agreement with previous experimental result (1~2 K/s).[16]

In order to generally describe the kinetics of phase transformation of amorphous alloys with a range of critical cooling rates, several theoretical approaches based on classical homogeneous nucleation theory have been undertaken.[10,11,17] However, there are large discrepancies between the theoretical model predictions and the experimental results. It has been shown that the critical cooling rate calculated by homogeneous nucleation theory was underestimated by four orders of magnitude against that obtained experimentally.[2] Irrespective of whether homogeneous nucleation or heterogeneous nucleation is operative, theoretical analyses require the knowledge of various thermophysical data such as viscosity, interface energy between liquid and crystalline phases, and heat of fusion. However, these values are not readily available, which makes the analyses of crystallization kinetics very difficult and less accurate. Nevertheless, our approach based on heterogeneous nucleation theory can overcome such problems. The main difference between heterogeneous and homogeneous nucleation theories is that the former considers the effect of heterogeneous nucleation sites with the unknown parameters $S_V$ (surface area of the catalyst in a unit volume) and $f(\theta)$ (shape factor) in nucleation equations. When the experimentally obtained thermal analysis data (i.e., nucleation temperatures at two different cooling rates) are substituted into nucleation equations, the values of $S_V$ and $f(\theta)$ can be obtained by graphical method and multiple regression using computer simulation. In our model, based on the heterogeneous nucleation theory, $S_V$ and $f(\theta)$ are self-adjusted depending on the values of input nucleation parameters. Since these input nucleation parameters are experimentally obtained by thermal analyses, they already reflect the effect of nucleation parameters. When different values of thermophysical properties are used, they vary accordingly, resulting in only a minor change in crystallization kinetics. Therefore, $S_V$ and $\theta$ should can be regarded as effective parameters. Afore-mentioned results indicate that our approach can be applied to the analyses of crystallization kinetics of continuously cooled bulk amorphous alloys with a wide range of critical cooling rates, despite the lack of thermophysical properties needed for the calculation.

## 3. Parameter for Glass Forming Ability

Glass formation is a competing process between the liquid and crystalline phases. Based on the analytic method of the crystallization kinetics of amorphous alloys, a new parameter for GFA can be suggested. Figure 3 shows the schematic diagram that explains the effect of GFA for the difference of nucleation temperatures $\Delta T_n$ on continuous cooling at different cooling rates. The C-shaped CCT curve implies that the alloy with higher GFA has a nose of CCT curve shifted to longer times, and thus exhibits a larger difference in nucleation temperatures between any two different coolings. If $\Delta T_n$ is normalized with liquidus temperature $T_l$, a new
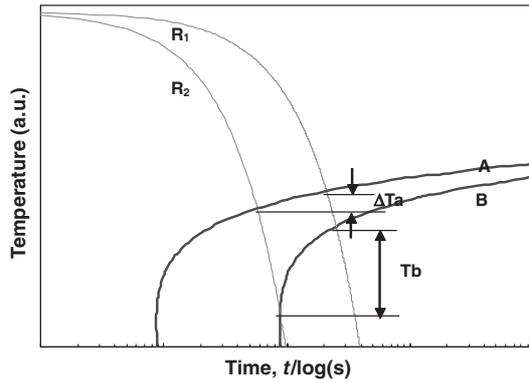
Fig. 3 Schematic diagram of critical cooling rate $R_c$ for the differences of nucleation temperatures $\Delta T_n$ between two cooling rates: $R$ ($R_1 < R_2$) on continuous cooling is a cooling rate. A and B are CCT diagrams with different critical cooling rate $R_c$ ($R_{cA} > R_{cB}$). $\Delta T$ ($\Delta T_a < \Delta T_b$) is a difference of nucleation temperatures.

parameter $\Delta T_{rn}$ (reduced difference of nucleation temperatures) for GFA can be expressed as,

$$\Delta T_{rn} = (T_{n1} - T_{n2})/T_l = \Delta T_n/T_l \qquad (1)$$

where $T_{n1}$ and $T_{n2}$ are the nucleation temperatures at two different cooling rates of $R_1$ and $R_2$, respectively. Table 1 summarizes the reduced difference of nucleation temperatures $\Delta T_{rn}$ and the previous experimental critical cooling rates $R_c$ for the cases of $Mg_{65}Cu_{25}Gd_{10}$, $Mg_{65}Cu_{25}Y_{10}$, and $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$ amorphous alloys containing $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. The values of $\Delta T_{rn}$ in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Mg_{65}Cu_{25}Gd_{10}$ alloys are much larger than those of $Mg_{65}Cu_{25}Y_{10}$ and $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$ alloys, which means that the GFA of the former materials is much better than the latter ones. As shown in Table 1, the values of $\Delta T_{rn}$ were in good agreement with the previous experimental data of critical cooling rates.

The introduction of $\Delta T_{rn}$ as a new parameter for estimating GFA is more standard than the traditional methods of using the parameters such as the reduced glass transition temperature $T_{rg}$, the supercooled liquid region $\Delta T_x$, and $\gamma$ ($= T_x/(T_g + T_l)$).[6] It has been shown that $T_{rg}$ and $\Delta T_x$ have contradicting trends with GFA in many alloy systems.[6–9] This might be due to the fact that these parameters by traditional method are expressed in terms of $T_g$ and $T_x$, which are obtained during heating. Since the glass formation is a competing process between liquid phase and crystalline phases during cooling, these parameters, in principle, are

related with the glass state stability, not with the glass forming ability. Therefore, it is more desirable to express GFA in terms of $T_n$, because an amorphous state is acquired in the kinetic process of continuous cooling from a liquid state. From this point of view, it is believed that the new parameter $\Delta T_{rn}$ is more reliable for GFA than the other parameters.

## 4. Model for Predicting Critical Cooling Rate

As stated in section 3, $\Delta T_{rn}$ has been defined as a new parameter for GFA of amorphous alloys. If the critical cooling rate $R_c$, which is the most effective factor for GFA, can be related with the parameter $\Delta T_{rn}$, we can simply calculate $R_c$ of amorphous alloys without previous knowledge of thermophysical properties in the nucleation and growth theory. By simplifying and approximating the equation based on the heterogeneous nucleation theory, the relationship between $R_c$ and $\Delta T_{rn}$ is obtained as:

$$\ln R_c = C_1(1/\Delta T_{rn}) - C_2 \qquad (2)$$

where $C_1$ and $C_2$ are kinetic constants depending on cooling rates. These constants were obtained from the results of the kinetic approach for various alloys. At different cooling rates of 5 and 20 K/min, the values of $C_1$ and $C_2$ are 0.023906 and 0.8178, respectively. Substituting the data of Table 1 into eq. (2), $R_c$ of various alloys has been calculated. As shown in Table 2, the calculated $R_c$ values were in good agreement with those measured in the previous experiments and those calculated from our crystallization approach based on the heterogeneous nucleation theory. It can be concluded that our model can accurately predict $R_c$ value of amorphous alloys from only two DTA experimental data.

## 5. Summary

Crystallization behavior of amorphous alloys can be expressed by the heterogeneous nucleation theory coupled with thermal analysis data. Based on this crystallization kinetic approach, the critical cooling rate, TTT diagram, and CCT diagram of amorphous alloys have been calculated. A new parameter $\Delta T_{rn}$ (reduced difference of nucleation temperatures) for GFA has been suggested with simple DTA data at two different cooling rates. It accurately described the GFA of amorphous alloys very well. An equation of critical cooling rate related with the new parameter for the glass formation is suggested as follows:

Table 1 DTA data of amorphous alloys: liquidus temperature $T_l$, nucleation temperatures $T_n$ and difference of nucleation temperatures $\Delta T_n$ at cooling rates of 5 K/min and 20 K/min, calculated reduced difference of nucleation temperatures $\Delta T_{rn}$, and reported critical cooling rates $R_c$.

| Alloys | Liquidus temperature, $T_l$/K | Nucleation temperature, $T_n$/K | | $\Delta T_n$, T/K | $\Delta T_{rn}$ ($\times 10^2$) | Critical cooling rate, $R_c$/K·s$^{-1}$ [ref.] |
|---|---|---|---|---|---|---|
| | | at 5 K/min | at 20 K/min | | | |
| $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ | 993 | 918 | 905.9 | 12.1 | 1.179 | 1–2[16] |
| $Mg_{65}Cu_{25}Gd_{10}$ | 755 | 716.6 | 704.8 | 11.8 | 1.562 | ∼ 1[18] |
| $Mg_{65}Cu_{25}Y_{10}$ | 772 | 732.5 | 728.3 | 4.2 | 0.544 | ∼ 50[19] |
| $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$ | 1174 | 1121.6 | 1117 | 4.6 | 0.392 | < 250[20] |

Table 2  Comparison of reduced differences of nucleation temperatures $\Delta T_m$, the reported critical cooling rates $R_c$, the previous simulated critical cooling rates, and the calculated critical cooling rates from Eq. 2 for amorphous alloys ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$, $Mg_{65}Cu_{25}Gd_{10}$, $Mg_{65}$-$Cu_{25}Y_{10}$, and $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$).

| Alloys | $\Delta T_m$ ($\times 10^2$) | $R_c$ (Ref.)/ $K \cdot s^{-1}$ | $R_c$ (Sim.)/ $K \cdot s^{-1}$ | $R_c$ (Eq. 2)/ $K \cdot s^{-1}$ |
|---|---|---|---|---|
| $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ | 1.179 | 1–2[16] | 1.7[2] | 3.2 |
| $Mg_{65}Cu_{25}Gd_{10}$ | 1.562 | $\sim 1$[18] | 1.7[21] | 2 |
| $Mg_{65}Cu_{25}Y_{10}$ | 0.544 | $\sim 50$[19] | 56[21] | 36 |
| $Cu_{47}Ti_{33}Zr_{11}Ni_6Si_1Sn_2$ | 0.392 | $< 250$[20] | 140[21] | 197 |

$$\ln R_c = C_1(1/\Delta T_m) - C_2$$

The prediction has been in good agreement with the previous experimental results. Based on this model, we can estimate critical cooling rates of amorphous alloys from simple DTA experimental data without previous knowledge of parameters in kinetic theory.

## Acknowledgments

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