RELAXATION BEHAVIOR OF Ca-BASED BULK METALLIC GLASSES (POSTPRINT)

Daniel B. Miracle
AFRL/RXCM

Oleg N. Senkov
UES, Inc.

APRIL 2014
Interim Report

Distribution Statement A. Approved for public release; distribution unlimited. See additional restrictions described on inside pages

STINFO COPY

© 2009 The Minerals, Metals & Materials Society and ASM International
NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

Qualified requestors may obtain copies of this report from the Defense Technical Information Center (DTIC) (http://www.dtic.mil).

AFRL-RX-WP-JA-2015-0118 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

//Signature//
MICHEAL E. BURBA, Project Engineer
Metals Branch
Structural Materials Division

//Signature//
DANIEL J. EVANS, Chief
Metals Branch
Structural Materials Division

//Signature//
ROBERT T. MARSHALL, Deputy Chief
Structural Materials Division
Materials And Manufacturing Directorate

This report is published in the interest of scientific and technical information exchange and its publication does not constitute the Government’s approval or disapproval of its ideas or findings.
**ABSTRACT**

The relaxation behavior of Ca-based bulk metallic glasses was determined in the glass transition region using differential scanning calorimetry (DSC) with heating rates from 1 to 160 K/min. The activation enthalpy of structural relaxation and the fragility index m were found to be smaller in the glassy state (onset of the glass transition) than in the supercooled liquid state (end of glass transition). The Ca-based glass-forming liquids showed strong behavior of the relaxation time, with the fragility indexes m in the range of 33 to 40. The strong liquid behavior implies sluggish kinetics of crystallization in the supercooled liquid region and explains the very good glass-forming ability (GFA) of these alloys. The critical cooling rate for amorphization R of the Ca-based bulk metallic glasses was estimated to be in the range of 0.3 to 10 K/s, which is similar to R_c values for the best Pd- and Zr-based metallic glass-forming alloys discovered so far.
Relaxation Behavior of Ca-Based Bulk Metallic Glasses

OLEG N. SENKOV and DANIEL B. MIRACLE

The relaxation behavior of Ca$_{60}$Mg$_{20}$Zn$_{20}$, Ca$_{60}$Mg$_{20}$Cu$_{20}$, Ca$_{65}$Mg$_{15}$Zn$_{20}$, Ca$_{90}$Mg$_{20}$Cu$_{30}$, and Ca$_{55}$Mg$_{18}$Zn$_{11}$Cu$_{16}$ bulk metallic glasses was determined in the glass transition region using differential scanning calorimetry (DSC) with heating rates from 1 to 160 K/min. The activation enthalpy of structural relaxation and the fragility index $m$ were found to be smaller in the glassy state (onset of the glass transition) than in the supercooled liquid state (end of glass transition). The Ca-based glass-forming liquids showed strong behavior of the relaxation time, with the fragility indexes $m$ in the range of 33 to 40. The strong liquid behavior implies sluggish kinetics of crystallization in the supercooled liquid region and explains the very good glass-forming ability (GFA) of these alloys. The critical cooling rate for amorphization $R_c$ of the Ca-based bulk metallic glasses was estimated to be in the range of 0.3 to 10 K/s, which is similar to $R_c$ values for the best Pd- and Zr-based metallic glass-forming alloys discovered so far.

I. INTRODUCTION

Depending on the temperature dependence of the relaxation time $\tau$ (or, equivalently, the viscosity $\eta = G\omega$, where $G$ is the dynamic shear modulus) in the temperature range between $T_g$ and $T_m$, where $T_g$ is the glass transition temperature and $T_m$ is the melting (usually liquidus) temperature, glass-forming liquids are divided into strong and fragile liquids. When the logarithm of the relaxation time of a supercooled liquid is plotted vs an inverse absolute temperature, $T$, reduced by $T_g$ (i.e., $\log(\tau) vs T/T_g$), all glass-forming liquids have the same relaxation time of $\tau_g = 10^3$ s at $T = T_g$ (in accord to this definition of $T_g$). With an increase in temperature above $T_g$, liquids with strong directional bonding and high stability of intermediate range order, such as silica or germania, show almost a linear, Arrhenius, dependence of $\log(\tau)$ on $T_g/T$ over the entire temperature range above $T_g$. These liquids are called strong liquids. At the same time, molecular liquids and many metallic glasses, which lack a strong directional bonding character and therefore possess a high configurational degeneracy and suffer rapid degradation of intermediate range order above $T_g$, show a very rapid decrease in $\log(\tau)$ with a decrease in $T_g/T$ in the temperature range of $T_g \leq T \leq T_m$ and a weak dependence above $T_m$. These liquids are called fragile liquids. Examples of extremely fragile liquids are o-terphenyl, toluene, pure metals, and marginal metallic glasses.

Stronger liquids are generally better glass formers because they have higher viscosity/relaxation time at $T < T_m$ and therefore slower kinetics of crystallization, than more fragile liquids.[2,4] Almost all bulk metallic glasses show intermediate fragile behavior.[5] Slow kinetics of crystallization due to high viscosity/high relaxation time of supercooled liquid can also be important for enhancing the GFA of bulk metallic glasses.

The fragile behavior of supercooled glass-forming liquids can generally be described by an empirical Vogel–Fulcher–Tamman (VFT) equation:[6]

$$\tau = \tau_\infty \exp[A/(T - T_o)]$$

where $\tau_\infty$, $A$, and $T_o$ are the fitting parameters. An approach to quantify liquid fragility defines a fragility index $m$ as the slope of the $\log_{10} \tau$ (or $\log_{10} \eta$) $vs T_g/T$ curve near $T_g$.[7]

$$m = \frac{d \log_{10} \tau}{d (T_g/T)} \bigg|_{T = T_g} \equiv \frac{d \log_{10} \eta}{d (T_g/T)} \bigg|_{T = T_g}$$

According to this definition, more fragile liquids have higher $m$ values.

Since its introduction in 1993, the fragility index $m$ has become an important material constant, which has been found to correlate with other glass properties, such as vibrational properties of the harmonic glassy dynamical,[6] Poisson's ratio,[9,10] jump in the heat capacity at $T_g$,[11,12] and GFA.[4,13] For example, the critical cooling rate for amorphization, $R_c$, was found to increase with an increase in the fragility index, $m$, obeying the following relation:[4]

$$\log(R_c) = 11.8 - 694/[32 + m(1/T_{rg} - 1)]$$

where $R_c$ is given in K/s and $T_{rg} = T_g/T_m$ is the reduced glass transition temperature.

Although $m$ describes the viscous behavior of a supercooled liquid near $T_g$, recent analysis[14] has shown

---

OLEG N. SENKOV, Senior Scientist, is with UES, Inc., Dayton, OH 45432. Contact e-mail: oleg.senkov@wpafb.af.mil DANIEL B. MIRACLE, Senior Scientist, is with the Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson AFB, OH 45433.

This article is based on a presentation given in the symposium “Bulk Metallic Glasses VI,” which occurred during the TMS Annual Meeting, February 15 19, 2009, in San Francisco, CA, under the auspices of TMS, the TMS Structural Materials Division, TMS/ASM: Mechanical Behavior of Materials Committee.

Article published online September 3, 2009

© The Minerals, Metals & Materials Society and ASM International 2009
that, together with other experimentally accessible parameters, it can be used to describe the temperature dependence of viscosity in a wider temperature range:

$$\log(\eta) = 12 - n \frac{1 - \frac{T_g}{T}}{1 - \left(1 - \frac{\eta}{\eta_0}\right) \frac{T}{T_g}}$$  \[4\]

In Eq. [4],

$$n = m - \frac{1 - (1 - T_{rg}) \Delta C_p(T_g) / \Delta n}{1 + T_{rg} \Delta C_p(T_g) / \Delta n}$$

$\Delta C_p(T_g)$ is the heat capacity jump at $T_g$, and $\Delta S(T_m)$ is the entropy of fusion.

The preceding brief overview clearly indicates a significant importance of the fragility index $m$ for linking dynamic and thermodynamic properties of supercooled liquid and glassy states. From this perspective, it is critical to establish experimental procedures for measuring correct values of $m$ for different glass-forming liquids. Two main methods to measure $m$ are widely used. The first is the straightforward method of measuring the steepness of the log $\eta$ vs $T_g/T$ or log $\tau$ vs $T_g/T$ curve at $T_g$, in accordance with Eq. [2], using reliable viscosity or relaxation time data for the supercooled liquid state in the temperature range close to $T_g$. An extensive $m$ database compiled by this direct method is currently available for many oxide and organic liquids,[7,11,15] as well as for some metallic alloys.[10,16] The fragility index obtained by this method is called the kinetic fragility index and is identified as $m_k$.

The second method involves differential scanning calorimetry (DSC) at a constant heating (or cooling) rate $\phi$. This approach uses the fact that, upon heating, the glass transition represents the relaxation of the nonequilibrium glassy state into the equilibrium supercooled liquid state. The kinetics of the glass transition reflects the relationship between the relaxation time and temperature. When a higher heating rate $\phi$ is used, the calorimetric glass transition temperature $T_{cal}$ shifts to a higher temperature. This dependence of $T_{cal}$ on $\phi$ is used to calculate the activation enthalpy of structural relaxation, $\Delta H_g$, at the glass transition[17]

$$\Delta H_g = -R \frac{d \ln \tau}{d \left(\ln T_{cal}\right)}$$  \[5\]

where $R$ is the gas constant. The calorimetric fragility index $m_c$ is then often calculated as

$$m_c = \frac{\Delta H_g}{R T_{cal} \ln 10}$$  \[6\]

In Eq. [6], $T_{cal}$ is the calorimetric glass transition temperature determined at a referenced heating rate $\phi_{ref}$. The latter can be defined as $\phi_{ref} = \Delta T_g / \tau_g$, where $\Delta T_g = T_{ge} - T_{gs}$ is the temperature interval of the glass transition; $T_{ge}$ and $T_{gs}$ are the temperatures of the start and the end of the glass transition, respectively; and $\tau_g = 1000$ s. Equation [6] is equivalent to Eq. [2] only if $\Delta T_g$ is essentially independent of the heating rate, which is not always correct.[1,18] In general, use of the total relaxation time for the calorimetric glass transition, $\tau_{cal} = \Delta T_g / \phi$, instead of $\phi$, is more appropriate[19,20] and $m_c$ is calculated as the slope of log $\tau_{cal}$ vs $1/T_{cal}$ reduced by $T_{cal}^d$.

$$m_c = \frac{1}{T_{cal}^d} \frac{\Delta \log \tau_{cal}}{\Delta \left(1/T_{cal}\right)} T_{cal}$$  \[7\]

The $m_c$ values obtained by DSC are almost always smaller than the $m_k$ values obtained from viscosity/relaxation time measurements.[10,15,17] For example, $m_k = 50, 59$, and $54$ vs $m_c = 39, 52$, and 41 were reported for Zr$_{41}$Ti$_{14}$Cu$_{12.5}$Ni$_{8}$Be$_{2.5},$ Pd$_{39}$Ni$_{10}$Cu$_{30}$P$_{21}$, and Pd$_{40}$Ni$_{40}$P$_{20}$, respectively.[10] In our opinion, the reason of such discrepancy is the temperature of the onset of the glass transition, i.e., $T_{gs}$, as $T_{cal}$ in Eqs. [6] and [7]. Indeed, analysis of all experimental data on calorimetric measurements of $m_c$ for bulk metallic glasses reported to date shows that only the time dependence of $T_{gs}$ has been used. However, $T_{gs}$ corresponds to the glassy state, and therefore, $m_c$ determined in this way reflects the relaxation behavior of the glassy state, while $m_k$, by definition, reflects the relaxation behavior of a supercooled liquid state at $T_g$. We therefore suggest here that, in order to correctly determine the relaxation behavior of a supercooled liquid near $T_g$ in DSC experiments, the temperature of the end of the glass transition, i.e., $T_{ge}$, should be used as $T_{cal}$ in Eq. [6] or [7], because, within the glass transition range, this temperature most closely corresponds to the supercooled liquid state.

In this article, we report on the relaxation behavior of several Ca-Mg-Zn, Ca-Mg-Cu, and Ca-Mg-Zn-Cu bulk metallic glasses (BMGs) determined by DSC in the glass transition range. These relatively new amorphous metallic materials are based on two simple metals, Ca and Mg, have the lowest density among all BMGs discovered so far, and have excellent glass-forming ability (GFA).[21 27] The relaxation behavior of these materials in the glassy state, using $T_{ge}$ as $T_{cal}$, is shown to be stronger than in the supercooled liquid state, where $T_{cal}$ is given by $T_{ge}$. The fragile behavior of the Ca-based BMGs is compared with the behavior of other metallic and nonmetallic glasses/supercooled liquids. It is concluded that the Ca-based supercooled liquids are less fragile than other BMGs, and their fragility is comparable with the fragility of strong oxide glasses. The GFA of the Ca-based BMGs is estimated to be similar to the GFA of the best glass-forming Pd-based and Zr-based BMGs.

II. EXPERIMENTAL PROCEDURES

Five Ca-based glassy alloys were prepared by a Cu-mold casting method in the form of 4-mm-thick plates. The nominal alloy compositions, in atomic percent, are Ca$_{60}$Mg$_{25}$Zn$_{20}$, Ca$_{60}$Mg$_{25}$Cu$_{20}$, Ca$_{60}$Mg$_{15}$Zn$_{20}$, Ca$_{60}$Mg$_{15}$Cu$_{20}$, Ca$_{60}$Mg$_{15}$Zn$_{20}$,
Ca_{50}Mg_{20}Cu_{30}, and Ca_{55}Mg_{18}Zn_{11}Cu_{16}. The methods of the alloy preparation and casting, as well as some thermodynamic properties of these glassy alloys, were reported elsewhere. The DSC heating runs of the amorphous samples were conducted on a TA Instruments Q-1000 differential scanning calorimeter (TA Instruments, New Castle, DE) in the temperature range of 330 to 450 K, which covered the glass transition region, with heating rates of 1.0, 2.5, 5.0, 10, 20, 40, 80, 110, and 160 K/min. The temperatures \( T_{gs} \) and \( T_{ge} \), as well as \( \Delta T_g \), were determined at different heating rates using TA Universal Analysis version 4.2E software (TA Instruments, New Castle, DE). From the rate of structural relaxation at \( T_{gs} \) regions near the glass transition with the use of Eqs. [5] and [7], respectively.

III. RESULTS

Figure 1 illustrates a typical DSC scan at the heating rate of 20 K/min of the Ca_{50}Mg_{20}Cu_{30} BMG. The glass, glass transition, and supercooled liquid temperature regions are clearly identified. The glass transition starts at \( T_{gs} \) and ends at \( T_{ge} \), while the supercooled liquid region is terminated by crystallization at \( T_x \). More examples of DSC scans for the Ca-based BMGs can be found in previous publications.

The dependences of \( T_{gs} \) and \( T_{ge} \) on the heating rate for two Ca-based BMGs are shown in Figure 2. Both \( T_{gs} \) and \( T_{ge} \) increase and the temperature interval of the glass transition \( \Delta T_g \) decreases with an increase in the heating rate. From the dependences of \( T_{gs} \) and \( T_{ge} \) on the heating rate, the activation enthalpies of structural relaxation at the beginning \( \Delta H_{gs} \) and the end \( \Delta H_{ge} \) of glass transition were calculated using Eq. [5], and their values are given in Table I. The \( m_c \) values calculated with Eq. [6] are also given in this table. It can be seen that the ternary Ca-based BMGs have almost the same \( \Delta H_{gs} \approx 121 \) to 127 kJ/mol, while the quaternary Ca_{55}Mg_{18}Zn_{11}Cu_{16} alloy has a slightly higher \( \Delta H_{gs} = 134 \) kJ/mol. The relaxation enthalpy increases with an increase in the volume fraction of the supercooled liquid, and at the end of the glass transition, \( \Delta H_{ge} = 211 \) to 229 kJ/mol for the ternary alloys and 225 kJ/mol for the quaternary alloy.

Figure 3 shows the dependences of the total relaxation time for the glass transition, \( \tau^{cal} = \Delta T_g / \phi \), on \( T_{gs} \) and \( T_{ge} \) plotted in Arrhenius coordinates, i.e., \( \log \tau^{cal} vs 1/T \). These dependences were fitted with the VFT Eq. [1], in which \( \tau_\infty = 10^{-14} \) s was assigned based on earlier observations that (1) for many glass-forming liquids, \( \tau_\infty \) is in the range of \( 10^{-15.5} \) to \( 10^{-12.5} \) s and (2) the VFT fit of the temperature dependence of the relaxation time near \( T_g \) is not very sensitive to the exact value of \( \tau_\infty \) in the given \( \tau_\infty \) range. The VFT fitting parameters \( A \) and \( T_o \) (Eq. [1]) for five Ca-based BMGs studied in this work are given in Tables II and III for the onset and the end
of the glass transition, respectively. Using these fitting parameters, the reference glass transition temperatures $T_{g}^{ref}$ and $T_{g}^{ref}$ for the onset and the end of the glass transition, respectively, were determined, using Eq. [1], as the temperatures at which $^{cal}_{g} = 1000$ s; i.e.,

$$T_{g}^{ref} = T_o + A/(17\ln 10) \approx T_o + 0.0255A$$

Finally, the fragility index $m_c$ was calculated for the onset and the end of the glass transition using Eq. [7] and the VFT fitting curves (Eq. [1]):

$$m_c = \frac{A}{T_o^{ref} - T_o^{c}} \ln 10$$

The calculated $T_{g}^{ref}$ and $m_c$ values for the Ca-based BMGs at the onset and the end of the glass transition are tabulated in Tables II and III, respectively.

IV. DISCUSSION

The results reported in this work clearly indicate that the relaxation behavior of Ca-based BMGs in the glass transition region is different at the onset and the end of the glass transition. The enthalpy of the structural relaxation $\Delta H_g$ and the fragility index $m_c$ were found to be smaller at the onset than at the end of the glass transition (Tables I through III). The parameters of the VFT Eq. [1] are also different so that $A$ is higher and $T_o$ is smaller for relaxation at the onset than at the end of the glass transition (compare Tables II and III). Taking into account that the liquid fragility increases with an increase in $m$ and a decrease in $T_o/T_g$, one can conclude that the Ca-based BMGs show conversion from non-Arrhenius (fragile) behavior of supercooled liquid to near-Arrhenius behavior of glass in the temperature region of the glass transition.

A similar transition from a steep temperature dependence of viscosity/relaxation time of supercooled liquid to the weaker dependence of respective glass has been earlier reported for several fragile organic liquids[29,30] as well as for metallic glasses.[19,31,32] For example, Figure 4 illustrates the temperature dependence of the viscosity of a-naphthyl benzene (TzNB).[29] The supercooled liquid of this organic glass former shows highly non-Arrhenius (fragile) behavior of the viscosity, with the fragility index $m_k = 76$ and the relaxation activation enthalpy $\Delta H_g \approx 485$ kJ/mol. At the same time, viscosity of the glass measured below $T_g$ shows much weaker, near Arrhenius, temperature dependence with $m_k = 28$ and the relaxation activation enthalpy $\Delta H_g \approx 179$ kJ/mol. Two other examples of the weaker temperature dependence of viscosity of the glass than the respective supercooled liquid have been reported for Zr$_{46.8}$T$_{18.2}$Cu$_{7.5}$Ni$_{10}$Be$_{27.5}$ (Figure 3 in Reference 19) and Mg$_{65}$Cu$_{25}$Y$_{10}$ (Figure 8 in Reference 31) amorphous metallic alloys. In both cases, a rapid, non-Arrhenius,
increase in the liquid viscosity with a decrease in the temperature, which can be described by the VFT Eq. [1], was observed. At the same time, the viscosity of a nonequilibrium glassy state was reported to show a much weaker temperature dependence, so that the difference between the equilibrium and nonequilibrium viscosities increased with a decrease in the temperature. From the slopes of log $\eta$ vs $1/T$ dependences near $T_g$, [19,31] we estimated the fragility indexes $m_{\text{e}}$ for the supercooled liquid and glassy states (i.e., for equilibrium and nonequilibrium amorphous states) to be 46.0 and 17.0 for the Zr-based alloy and 50.0 and 30.5 for the Mg-based alloy, respectively. The less viscous behavior and a weaker temperature dependence of the viscosity of the nonequilibrium glass relative to the equilibrium liquid at $T < T_g$ were attributed to the frozen-in excess free volume in the glass. [19,33]

Table II. Fitting Parameters of the VFT Equation [1] for the Onset of the Glass Transition of Five Ca-Based BMGs

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\tau_{s}$ (s)</th>
<th>$A_s$ (K)</th>
<th>$T_{o,s}$ (K)</th>
<th>$r_s^2$</th>
<th>$T_{gs}^{\text{ref}}$ (K)</th>
<th>$m_{c,s}$ (Eq. [7])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{55}$Mg$</em>{18}$Zn$<em>{11}$Cu$</em>{16}$ &amp; 10$^{-14}$</td>
<td>9138</td>
<td>108.3</td>
<td>0.99866</td>
<td>341.7</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>11,306</td>
<td>61.3</td>
<td>0.99977</td>
<td>350.1</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Cu$_{30}$ &amp; 10$^{-14}$</td>
<td>11,503</td>
<td>59.1</td>
<td>0.99963</td>
<td>335.0</td>
<td>20.4</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>12,231</td>
<td>50.8</td>
<td>0.99731</td>
<td>363.3</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{65}$Mg$</em>{15}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>10,726</td>
<td>85.8</td>
<td>0.99921</td>
<td>359.8</td>
<td>22.3</td>
<td></td>
</tr>
</tbody>
</table>

*The coefficient of determination of the fit, $r^2$, and the calculated $T_{gs}^{\text{ref}}$ (the onset temperature at which $\eta_{gs}^{\text{ref}}$  10$^3$ s) and $m_{c,s}$ (Eq. [7]) values are also given here. The subscript $s$ indicates that the parameters are associated with the onset (start) of glass transition.

Table III. Fitting Parameters of the VFT Equation [1] for the End of the Glass Transition of Five Ca-Based BMGs

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\tau_{s}$ (s)</th>
<th>$A_s$ (K)</th>
<th>$T_{o,s}$ (K)</th>
<th>$r_s^2$</th>
<th>$T_{ge}^{\text{ref}}$ (K)</th>
<th>$m_{c,e}$ (Eq. [7])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{55}$Mg$</em>{18}$Zn$<em>{11}$Cu$</em>{16}$ &amp; 10$^{-14}$</td>
<td>5985</td>
<td>206.8</td>
<td>0.99847</td>
<td>359.7</td>
<td>40.0</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>7582</td>
<td>190.4</td>
<td>0.99481</td>
<td>384.1</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Cu$_{30}$ &amp; 10$^{-14}$</td>
<td>7693</td>
<td>196.5</td>
<td>0.9985</td>
<td>393.0</td>
<td>34.0</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{60}$Mg$</em>{20}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>8050</td>
<td>197.1</td>
<td>0.98727</td>
<td>402.8</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{65}$Mg$</em>{15}$Zn$_{20}$ &amp; 10$^{-14}$</td>
<td>6688</td>
<td>218.5</td>
<td>0.99749</td>
<td>389.4</td>
<td>38.7</td>
<td></td>
</tr>
</tbody>
</table>

*The coefficient of determination of the fit, $r^2$, and the calculated $T_{ge}^{\text{ref}}$ (the temperature of the end of the glass transition at which $\eta_{ge}^{\text{ref}}$  10$^3$ s) and $m_{c,e}$ (Eq. [7]) values are also given here. The subscript $e$ indicates that the parameters are associated with the end of the glass transition.

higher temperatures where the equilibrium (supercooled liquid state) can be achieved within the time governed by the heating rate. One can therefore conclude that the rate dependence of the end of the glass transition, $T_{ge}$, must be used in these DSC experiments for correct computation of properties of the supercooled liquid (e.g., $m_{c}$ and $\Delta H_g$). The onset of the glass transition cannot be used for this purpose, because $m_{c,s}$ and $\Delta H_{gs}$ values determined at $T_{gs}$ correspond to a nonequilibrium condition of the glass and, therefore, their values depend on the glass history. This explains why the $m_{c,e}$ values obtained in DSC heating experiments and related to the onset of the glass transition are almost always smaller than the $m_{c,s}$ values obtained from direct measurements of equilibrium viscosity/relaxation time of supercooled liquids. [10,15,17]

Another important observation of this work is that the fragility indexes calculated using Eq. [6] are about 10 to 20 pct smaller than those obtained with the use of Eq. [7]. This observation indicates that the temperature dependences of the DSC heating rate and the glass transition relaxation time are different, which is evidently due to the rate dependence of the glass transition width $\Delta T_g$. Indeed, as it was first discussed in Reference 1, $\frac{\Delta T_g}{\kappa} = \Delta T_g/\phi$ or $\frac{d\log \tau_g}{d\log \phi} = \frac{d\log \Delta T_g}{d\log \phi} - 1$. Therefore, Eqs. [6] and [7] for calculation of $m_{c}$ will be equivalent (i.e., $d\log \tau_g^{\text{ref}} = -d\log \phi$) only if the contribution from the $\Delta T_g$ containing term to $m_{c}$ is less than or compared to the experimental error (generally, <5 pct). Otherwise, Eq. [6] should not be used as it would provide incorrect $m_{c}$ values.

Figure 5 compares the fragile behavior of the relaxation time of the equilibrium Ca-based glass-forming
values for some other BMGs, which were estimated independently by two methods, (1) from experimental temperature-time-transformation (TTT) diagrams and (2) using Eq. [3], are also presented in this table for comparison. A rather good agreement between the $R_c$ values estimated by these two methods can be seen, indicating that Eq. [3] estimates the critical cooling rates for amorphization rather well (refer also to Reference 4). Therefore, the low $R_c$ values (about 0.2 to 10 K/s) predicted by this equation for the Ca-based glasses should also be considered reliable. Therefore, one can conclude that the GFA of the Ca-based BMGs is similar to that of the Pd- and Zr-based BMGs.

The excellent GFA of Ca-based BMGs indicates sluggish crystallization during solidification, as crystallization and glass formation are always competing processes; thus, glass is formed only when crystallization is suppressed during solidification. Crystallization is thermodynamically and kinetically driven, and it accompanies the atomic rearrangements from the disordered state of liquid to a long-range-ordered state of crystal. Recent thermodynamic analysis of the Ca-Mg-Zn alloy system by Gorsse et al. [3] showed that the GFA of these alloys generally improves with a decrease in the onset driving force for crystallization. Slow kinetics of crystallization due to high viscosity/high relaxation time of supercooled liquid can also be important for enhancing the GFA of bulk metallic glasses [3]. As stronger liquids generally have a higher viscosity/higher relaxation time between the melting and glass transition temperatures than more fragile liquids, the crystallization kinetics of the former (at the same driving force) are generally much slower, leading to enhanced GFA.

\[ \eta = \frac{G_m \Gamma}{k_B T} \]

Equation [3] estimates the critical cooling rate for amorphization $\Gamma$ for some other BMGs, which were estimated independently by two methods, (1) from experimental temperature-time-transformation (TTT) diagrams and (2) using Eq. [3], are also presented in this table for comparison. A rather good agreement between the $R_c$ values estimated by these two methods can be seen, indicating that Eq. [3] estimates the critical cooling rates for amorphization rather well (refer also to Reference 4). Therefore, the low $R_c$ values (about 0.2 to 10 K/s) predicted by this equation for the Ca-based glasses should also be considered reliable. Therefore, one can conclude that the GFA of the Ca-based BMGs is similar to that of the Pd- and Zr-based BMGs.

The excellent GFA of Ca-based BMGs indicates sluggish crystallization during solidification, as crystallization and glass formation are always competing processes; thus, glass is formed only when crystallization is suppressed during solidification. Crystallization is thermodynamically and kinetically driven, and it accompanies the atomic rearrangements from the disordered state of liquid to a long-range-ordered state of crystal. Recent thermodynamic analysis of the Ca-Mg-Zn alloy system by Gorsse et al. [3] showed that the GFA of these alloys generally improves with a decrease in the onset driving force for crystallization. Slow kinetics of crystallization due to high viscosity/high relaxation time of supercooled liquid can also be important for enhancing the GFA of bulk metallic glasses [3]. As stronger liquids generally have a higher viscosity/higher relaxation time between the melting and glass transition temperatures than more fragile liquids, the crystallization kinetics of the former (at the same driving force) are generally much slower, leading to enhanced GFA.

\[ \frac{T_g}{T_m} \approx 0.55 \text{ to } 0.7 \]
heating rates from 1 to 160 K/min. The temperatures of the start \( T_{gr} \) and the end \( T_{gr} \) of the glass transition increase, while the glass transition temperature width \( \Delta T_g = T_{gr} - T_{gs} \) decreases with an increase in the heating rate. Such behavior allows analysis and comparison of the temperature dependence of the relaxation time in the nonequilibrium glassy state near the onset of the glass transition and in the equilibrium supercooled liquid state near the end of the glass transition.

The temperature dependences of the relaxation time at the onset and at the end of the glass transition are different. The activation enthalpy of structural relaxation \( H_g \) and the fragility index \( m_c \) are smaller in the glassy state than in the supercooled liquid state. The smaller \( H_g \) indicates easier activation of the structural relaxation in the glassy state than in the supercooled liquid state at temperatures near and below \( T_g \), which explains the reduced values of the relaxation time and viscosity of glass relative to the supercooled liquid in this temperature range.

It was concluded that the heating rate dependence of the end of the glass transition should be used to correctly analyze the relaxation behavior of the supercooled liquid. The onset glass transition temperature cannot be used to analyze the equilibrium behavior, because in this condition, almost 100 pct of the material is in a nonequilibrium glassy state.

The Ca-based glass-forming liquids show strong behavior of the relaxation time, with the fragility indexes \( m_c \) in the range of 33 to 40. The strong liquid behavior implies sluggish kinetics of crystallization in the supercooled liquid region and can explain the very good GFA of these alloys. The critical cooling rate \( R_c \) of the Ca-based bulk metallic glasses was estimated to be in the range of 0.3 to 10 K/s, which is similar to \( R_c \) values for the best Pd- and Zr-based metallic glass-forming alloys discovered so far.

**ACKNOWLEDGMENTS**

The technical support from J.M. Scott (sample preparation) and S.V. Senkova (DSC experiments) is very much appreciated. This work was financially supported through the Air Force Office of Scientific Research (Dr. J. Fuller, Program Manager) and the Air Force Research Laboratory On-site Contract No. FA8650-04-D-5235 (UES, Inc.).

**REFERENCES**


