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# Fragility and glass-forming ability of the Ca–Mg–Cu system

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## Abstract

Elastic moduli of the glass and fragility of the corresponding supercooled liquid were found to be correlated in recently published results. In the present work, compositions within the Ca–Mg–Cu system are used to study the relationships between liquid fragility, glass-forming ability and elastic properties. The correlation between liquid fragility and elastic properties already observed for glasses in general is found to hold in this particular system. More extensive work should be done in order to obtain conclusive results. However, if such a correlation turns out to be general in metallic systems, it will be a powerful criterion in choosing candidate compositions for new bulk metallic glasses.

*Keywords:* Amorphous materials; Liquid quenching; Calorimetry

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## 1. Introduction

Over the last few years many new bulk-metallic-glass (BMG) compositions have been produced, thereby increasing expectations of the structural applications of these alloys. Production of BMGs via melt casting is strongly limited by the glass-forming ability (GFA) of the alloy. The factors influencing GFA are then a subject of interest.

One of the principal factors affecting the GFA is the nature of the supercooled liquid. Near the glass-transition temperature $T_g$ the properties of the liquid can be discussed in terms of the fragility parameter $m$ that was first defined by Böhmer et al. [1], and given by

$$m = \left.\frac{\mathrm{d}\log_{10}\tau}{\mathrm{d}T_g/T}\right|_{T=T_g} \qquad (1)$$

where $T$ is the temperature and $\tau$ is a structural-relaxation time. A *strong* liquid behaviour (small $m$) is expected to promote GFA; the high viscosity throughout the supercooled liquid region hinders nucleation and growth of crystalline phases. Indeed, BMGs are relatively strong liquids in the Angell plot [2], with $m = 30$–$60$, while conventional metallic glasses are commonly in the medium-fragile range, with $m = 50$–$100$ [3,4]. However, high GFA and strong-liquid behaviour are not closely related: the best metallic glass-forming alloy ($Pd_{40}Ni_{10}Cu_{30}P_{20}$, at.%) has $m = 59$ and then is on the fragile end among the BMG-forming alloys.

Recent works have related the fragility of the supercooled liquid to the number of components in the alloy [5] and to the elastic constants of the glass [6,7]. In the latter case, it seems that the Poisson ratio ($\nu$) of the glass, or in similar way the ratio between bulk ($K$) and shear ($G$) moduli, is directly related to the fragility of the liquid: the higher $K/G$, the more fragile the liquid.

Lewandowski et al. [8] showed a direct relationship between the Poisson ratio of BMGs and their ductile-brittle behaviour. Hence, there may be a connection between the liquid fragility (and so the GFA) and the mechanical properties of metallic glasses. If a significant relationship were confirmed, it would be a key point in determining the applicability of BMG compositions as structural materials.

The aim of this work is to check the general correlation between liquid fragility and elastic moduli described in Refs. [6,7] in a single compositional system. Ribbons of composition $Ca_{(30–60)}Mg_{(5–50)}Cu_{(5–60)}$ (nominal composition, at.%) were produced by rapid melt-quenching in a melt-spinner. This system was found to have high GFA around the $Ca_{50}Mg_{20}Cu_{30}$ composition [9]. Rapid quenching allowed us to obtain a wide set of compositions with amorphous structure around the BMG-forming composition. The liquid fragility was determined by

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Table 1
The values of $T_g$, $T_x$, $T_m$ and $T_l$ for the set of alloy compositions studied in this work

| Alloy no. | Composition (at.%) | Structure after quenching[a] | $T_g$ (°C) | $T_x$ (°C) | $T_m$ (°C) | $T_l$ (°C) | $T_l - T_m$ (°C) |
|---|---|---|---|---|---|---|---|
| 1 | $Ca_{49.5}Mg_{4.6}Cu_{45.9}$ | A/C | 109 | 148 | 351 | 535 | 184 |
| 2 | $Ca_{48.0}Mg_{10.7}Cu_{41.3}$ | A | 124 | 146 | 356 | 487 | 131 |
| 3 | $Ca_{48.9}Mg_{18.5}Cu_{32.6}$ | A | 128 | 156 | 353 | 411 | 58 |
| 4 | $Ca_{49.1}Mg_{29.0}Cu_{21.9}$ | A/C | – | 153 | 353 | 369 | 17 |
| 5 | $Ca_{51.0}Mg_{37.6}Cu_{11.4}$ | C | – | – | – | – | – |
| 6 | $Ca_{38.4}Mg_{3.7}Cu_{57.9}$ | A | 138 | 150 | 423 | 529 | 106 |
| 7 | $Ca_{38.8}Mg_{9.2}Cu_{52.0}$ | A | 123 | 145 | 374 | 500 | 126 |
| 8 | $Ca_{38.9}Mg_{18.1}Cu_{43.0}$ | A | 119 | 147 | 374 | 435 | 60 |
| 9 | $Ca_{40.3}Mg_{27.0}Cu_{32.7}$ | A/C | 125 | 143 | 375 | 376 | 1 |
| 10 | $Ca_{40}Mg_{40}Cu_{20}$[b] | C | – | – | – | – | – |
| 11 | $Ca_{30}Mg_{5}Cu_{65}$[b] | C | – | – | – | – | – |
| 12 | $Ca_{28.9}Mg_{8.2}Cu_{62.9}$ | A/C | 127 | 143 | 421 | – | – |
| 13 | $Ca_{28.7}Mg_{16.9}Cu_{54.4}$ | A | 123 | 155 | 371 | 432 | 61 |
| 14 | $Ca_{28.5}Mg_{26.5}Cu_{45.0}$ | A | 114 | 156 | 372 | 380 | 8 |
| 15 | $Ca_{30}Mg_{50}Cu_{20}$[b] | C | – | – | – | – | – |

The Tg and Tx values are obtained with a heating rate of 20 K min$^{-1}$

[a] A: amorphous; C: crystalline or partially crystalline; A/C: maybe partially crystalline.

[b] Nominal compositions instead of EDS results are quoted for these samples.

calorimetric methods while the elastic constants of the amorphous alloys were estimated from those of the pure elements in close-packed structures.

## 2. Experimental details

Pure Ca, Mg and Cu were melted in a BN crucible under argon atmosphere. Ribbons (with thickness between 90 ± 10 and 140 ± 10 μm) were produced by melt-spinning on a copper wheel with peripheral of 20 m s$^{-1}$ and other experimental conditions held constant. Table 1 lists the glasses produced; the quoted compositions were determined by energy-dispersive spectroscopy (EDS) in a JEOL-JSM 5800 low-vacuum scanning electron microscope. Amorphicity was assessed by X-ray diffraction in a Philips PW 1050/80 diffractometer (Cu Kα radiation).

The glass transition ($T_g$), crystallization ($T_x$), melting ($T_m$) and liquidus ($T_l$) temperatures were determined by calorimetric analysis in a TA-instruments Q1000 differential scanning calorimeter (DSC). The ribbons were annealed with different heating rates $Q$ ranging from 1 to 30 K min$^{-1}$ in order to determine $T_g$ and $T_x$ as a function of $Q$.

## 3. Results and discussion

Table 1 summarizes some of the results obtained. For alloys 1, 4, 9 and 12, X-ray analysis does not show any crystalline peaks, but the reduced area of the DSC exotherms indicates some degree of prior crystallization. The values of $T_g$, $T_x$, $T_m$ and $T_l$ quoted in Table 1 were obtained with $Q = 20$ K min$^{-1}$. In Fig. 1(a) a DSC scan of alloy 8 clearly shows the glass-transition, crystallization-onset and melting temperatures. There is an exothermic relaxation before the glass transition in most of the samples. From the results in Table 1 the position of a eutectic point in the ternary diagram can be deduced: the difference between liquidus and melting temperatures $T_l - T_m$ always decreases when approaching the composition $Ca_{40}Mg_{30}Cu_{30}$. This is consistent with the existence of a BMG-forming alloy around the nearby composition $Ca_{50}Mg_{20}Cu_{30}$ [9].

The fragility parameter $m$ of the alloys was calculated from the variation of $T_x$ with $Q$. At lower heating rates, the supercooled alloy has more time to relax and then both the glass transition and crystallization occur at lower temperatures. This kinetic behaviour can be used to measure the temperature dependence of a characteristic relaxation time [10,11]. At low $Q$, both $T_g(Q)$ and $T_x(Q)$ can be fitted by the Vogel–Fulcher–Tammann

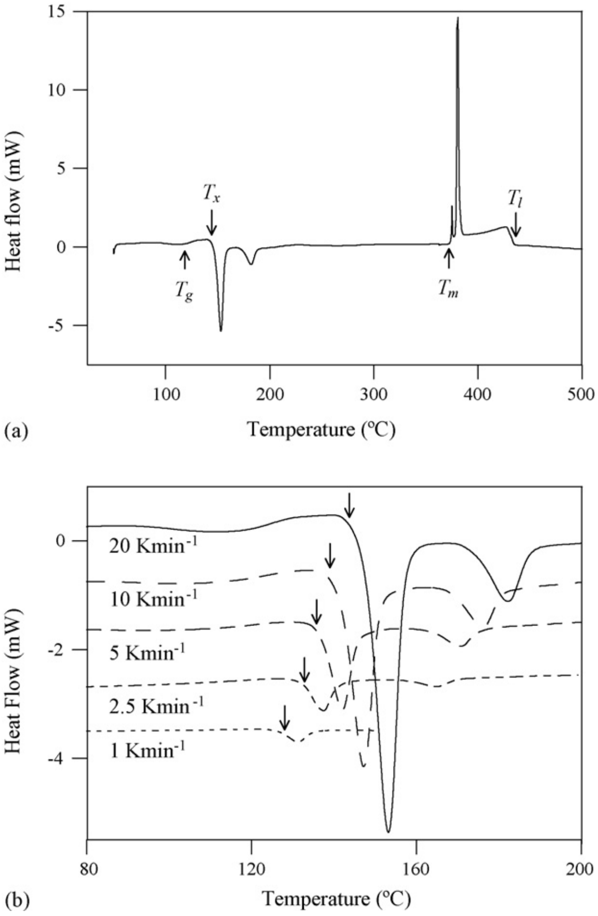

Fig. 1. (a) DSC curve for alloy 8 at $Q = 20$ K min$^{-1}$; (b) DSC curves for alloy 8 at different heating rates.

(VFT) equation [12]:

$$Q^{-1} = A \exp\left(\frac{DT_0}{T - T_0}\right) \tag{2}$$

where $D$, $A$ and $T_0$ are fitting parameters and $T$ is either $T_g$ or $T_x$ measured at heating rate $Q$. From the VFT fit the fragility parameter $m$ is calculated from

$$m = \frac{DT_0 T_{ref}}{(T_{ref} - T_0)^2 \ln 10} \tag{3}$$

where $T_{ref}$ is either $T_g$ or $T_x$ at the lowest heating rate $Q = 1\ \mathrm{K\,min^{-1}}$. The Ca–Mg–Cu alloys studied have $T_x$ close to $T_g$. At low $Q$ in many compositions, $T_g$ is difficult to determine because of the reduction of the calorimetric signal and/or the overlap between the glass transition and crystallization. Therefore, in this work fragility was calculated from the variation of $T_x$. In Fig. 1(b) the DSC scans at different $Q$ for sample 8 show clearly that $T_x$ is lowered as $Q$ is reduced.

Fig. 2 shows the variation of $Q^{-1}$ with the inverse crystallization temperature for some of the samples. The alloys with partially crystalline as-quenched structure were not considered in the fragility study. In a partially crystallized sample the glassy matrix and the whole ribbon may have different compositions. As seen in Fig. 2, all the analysed alloys have fragility values within the range $m = 26$–$36$. These values are similar to those obtained by calorimetric methods in other BMG-forming alloys [7,12] and characterize the Ca–Mg–Cu compositions as strong liquids. Here it is worth bearing in mind that the fragility values differ between viscosity and calorimetric measurements as well as between calorimetric methods using $T_g$ or $T_x$. Fragility values in the literature can be compared only with caution.

The elastic constants $E$ (Young modulus), $G$, $K$ and $\nu$ of amorphous metallic alloys are closely related to the values for the constituent elements in their close-packed structures. They can be estimated as [13]:

$$M^{-1} = \sum f_i M^{-1} \tag{4}$$

where $M$ denotes any elastic constant and $f_i$ the atomic percentage of the $i$th constituent element (for further work on this correlation, see [14]). This relationship works quite well in systems in which all the constituents are metallic elements, while there are significant deviations in systems containing P, B and Be. The values of the Poisson ratio predicted in this work using Eq. (4), are not claimed to be accurate, but they do provide a way of ranking the Ca–Mg–Cu alloys by their value of $\nu$ (or similarly by $K/G = 2(1+\nu)/3(1-2\nu)$).

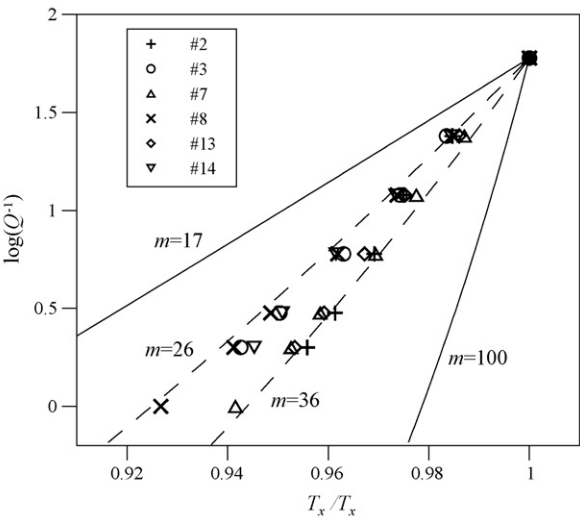

Fig. 2. An Arrhenius plot of the variation of the inverse DSC heating rate $Q^{-1}$ with the inverse crystallization temperature $T_x$ for alloys 2, 3, 7, 8, 13 and 14 in Table 1. The dashed and solid lines are VFT curves with different fragility values.

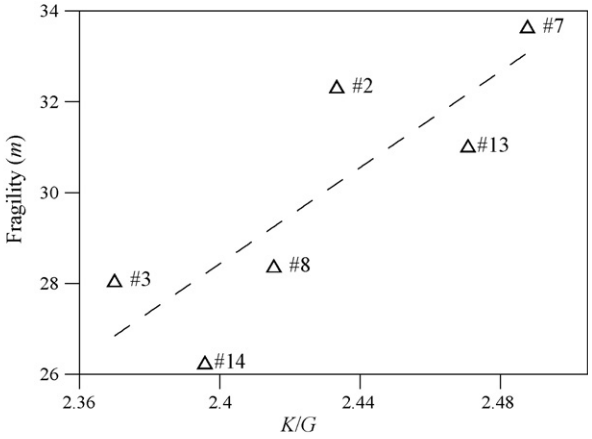

Fig. 3. Correlation between the fragility parameter $m$ and the estimated ratio of the bulk to shear moduli $K/G$ for the Ca–Mg–Cu glasses.

Fig. 3 shows the correlation between $m$ and $K/G$. As expected, the fragility of the liquid increases with the $K/G$ ratio of the alloy. The correlation shown in Fig. 3 is not by itself conclusive; for confirmation, it would be good to have more glass compositions and corresponding measurements of elastic moduli. However, the trend in Fig. 3 is consistent with similar, recently noted correlations both in metallic and general glasses [6,7].

Fragility and GFA are generally correlated in glasses. A low fragility (strong liquid) is expected to promote GFA. However, the number and relative stability of competing crystalline phases are also decisive in determining the GFA of a given alloy within a single compositional system. Indeed, no correlation can be made between GFA and fragility for the Ca–Mg–Cu system. The decrease of the liquid fragility with the increase of Mg concentration leads to partially crystalline as-quenched alloys beyond ∼20 at.% Mg.

## 4. Conclusions

The fragility of the supercooled liquid and the Poisson ratio of the corresponding glass have been found to be correlated in recent works. The present study of the Ca–Mg–Cu system shows a similar correlation within a single compositional system. The fragility parameters of compositions in the Ca–Mg–Cu system were calculated by means of calorimetric measurements.

The elastic constants of metallic glasses were estimated as a weighted average of the values of their constituent elements in their close-packed structures. Although further work would be desirable, it appears that the correlation between fragility and elastic moduli is general for metallic glasses. If verified, this would become a powerful tool when choosing compositions for possible new BMGs. A more detailed knowledge of the relationship between the elastic constants of the metallic components and both the GFA and the elastic constants of the glass can be of great value in guiding the selection of new BMG compositions with good mechanical properties for structural applications.

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