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1999 J. Phys.: Condens. Matter 11 3807

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# Compilation of the fragility parameters for several glass-forming metallic alloys

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Received 23 February 1999

**Abstract.** The fragility parameter,  $m$ , in the general classification scheme of glass-forming liquids has been estimated from data provided in the literature for viscosity measurements close to and below the calorimetric glass transition temperature for 21 metallic alloys consisting of ternary, quaternary and quinary alloys. These alloys are found to display an intermediate fragility strength with  $32 \leq m \leq 66$  and an average of  $m \approx 50$ . Of this group of alloys, the bulk metallic glass formers (those with critical cooling rates less than  $100 \text{ K s}^{-1}$ ) are stronger liquids with  $m$  lying between 30 and 40. There appears to be a general positive correlation between exceptionally good glass-forming ability and stronger dynamical behaviour of supercooled metallic liquids.

## 1. Introduction

It is well documented that, irrespective of chemical composition, the viscosity,  $\eta$ , of supercooled fluids increases dramatically by approximately 7 to 14 orders of magnitude between the melting temperature,  $T_m$ , and the glass transition temperature,  $T_g$ , where the relaxation time in the material becomes comparable to the timescale of a conventional laboratory experiment [1]. For many glass-forming liquids, the temperature dependence of  $\eta$  for temperature intervals lying between  $T_m$  and  $T_g$  can be described by the Vogel–Fulcher–Tammann (VFT) equation [2]:

$$\eta = \eta_0 \exp \left[ \frac{B}{T - T_0} \right] \quad (1)$$

where  $\eta_0$ ,  $B$  and  $T_0$  are fitting parameters and  $T$  is the temperature. Often over a narrower temperature range, especially near  $T_g$ ,  $\eta(T)$  can also be approximated very well by an Arrhenius equation where  $T_0 = 0$  in equation (1), and is given by

$$\eta = \eta_0 \exp \left[ \frac{E_a}{RT} \right] \quad (2)$$

where  $E_a$  is an activation energy and  $R$  is the gas constant.

For a limited number of supercooled liquids, such as  $\text{SiO}_2$  and  $\text{GeO}_2$  which have a three-dimensional tetrahedral network structure, the Arrhenius law can be used to fit  $\eta(T)$  over the entire temperature range between  $T_m$  and  $T_g$  [3]. All other glass-forming liquids exhibit varying degrees of departure from Arrhenius behaviour. These different temperature variations of the viscosity have been utilized by Angell and co-workers [1, 4, 5] to segregate the vast number of glass-forming materials into three broad categories: strong, intermediate and fragile liquids. Strong liquids are those with an Arrhenius temperature dependence of the viscosity,

while fragile liquids are more sensitive to thermal changes and display large deviations from Arrhenius behaviour.

In order to quantify the fragility (the degree of departure from an Arrhenius temperature dependence), Böhmer *et al* [5] have introduced a fragility parameter  $m$  defined as

$$m = \left. \frac{d \log_{10} \tau(T)}{dT_g/T} \right|_{T=T_g} \quad (3)$$

where  $\tau(T)$  is a characteristic temperature-dependent relaxation time. Since the viscosity is proportional to a structural relaxation time,  $m$  can be estimated by replacing  $\tau(T)$  with  $\eta(T)$  in equation (3). The fragility parameter is then a measure of the steepness of the slope of the viscosity curve at  $T_g$  when the temperature is scaled by  $T_g$ . If  $\eta(T)$  can be described by the Arrhenius equation, then

$$m = \frac{E_a}{RT_g \ln 10}. \quad (4)$$

Otherwise, if  $\eta(T)$  is given by the VFT equation, then

$$m = \frac{BT_g}{(T_g - T_0)^2 \ln 10}. \quad (5)$$

For strong liquids,  $m < 30$  with a lower limit of  $\approx 16$ . For example,  $\text{SiO}_2$  and  $\text{GeO}_2$  have  $m \approx 20$  at  $T_g$  [5]. Fragile liquids, on the other hand, are associated with  $m \geq 100$ . Böhmer and co-workers have compiled the fragility parameters for approximately 70 glass formers consisting of simple and complex covalent molecular liquids, polymers, ionic melts, oxides and alcohols [5]. However, no data on metallic alloys have been included in this compilation.

An initial attempt to investigate the value of  $m$  for glass-forming metallic alloys was conducted by Komatsu [6]. He calculated  $m$  for 11 metallic alloys consisting of binary and ternary systems by using VFT fits to viscosity data near  $T_m$  provided by Davies [7]. The VFT fits were extrapolated to determine the temperature corresponding to  $\eta = 10^{12}$  Pa s which was taken to be  $T_g$ . This analysis gave fragility parameters in the range  $86 \leq m \leq 121$  which would imply that metallic alloys appear to be very fragile liquids. The method employed above, however, is open to criticism since it is well known that a single set of parameters for the VFT equation is not able to fit the viscosity of non-strong liquids over the entire temperature range between  $T_m$  and  $T_g$  [8–10]. Two different sets of parameters are required for the domains of low (close to  $T_g$ ) and high (close to  $T_m$ ) temperature. Thus the values of  $m$  given above for the metallic alloys are unreliable.

In order to obtain more reliable estimates of the fragility parameter for metallic alloys, a search of the literature for viscosity data in the temperature range close to and below the calorimetric  $T_g$  has been conducted. The values of  $m$  calculated from these viscosity data are presented in this short paper. The investigation was carried out in order to determine whether there are any wide variations in the dynamic behaviour of glass-forming metallic alloys or whether instead there is a general inclination towards either the strong or fragile limits in the Angell classification scheme mentioned earlier.

## 2. Results and discussion

The fragility parameter  $m$  has been calculated for several glass-forming metallic alloys using equation (4) or equation (5) by employing experimental fits in the literature to viscosity data over intervals which include measurements that lie within several orders of magnitude above

$\eta = 10^{10}$  Pa s. Since  $m$  is a measure of the steepness of the viscosity curve at  $T_g$ , its value is dependent on the definition of  $T_g$ . In order to make a uniform comparison then,  $m$  has been evaluated at the temperature corresponding to the point of inflection (point of steepest ascent) in the specific heat curve during a differential scanning calorimetry (DSC) scan at a heating rate of  $20 \text{ K min}^{-1}$ . This calorimetric glass transition temperature will be denoted by  $T_g^c$  and the corresponding fragility parameter by  $m_c$ . These values, which were obtained from tabulated data or figures in cited references, are tabulated in table 1 for 21 metallic alloys. An alternative, fashionable definition of  $T_g$  is as the temperature at which  $\eta = 10^{12}$  Pa s [1]. We have also estimated this temperature, denoted by  $T_g^v$ , for those alloys for which the value of  $\eta_0$  in equation (1) or (2), which is needed to determine  $T_g^v$ , has been provided in the respective references. This temperature and its associated fragility parameter, labelled as  $m_v$ , are also listed in table 1. As can be seen in this table,  $T_g^c > T_g^v$  since the viscosity at  $T_g^c$  is approximately one to two orders of magnitude lower than  $10^{12}$  Pa s.

**Table 1.** The fragility parameters,  $m_c$  and  $m_v$ , for 21 metallic glass formers calculated respectively at the calorimetric glass transition temperature  $T_g^c$  for a heating rate of  $20 \text{ K min}^{-1}$  and at the temperature  $T_g^v$  corresponding to  $\eta = 10^{12}$  Pa s. All values have been rounded to the nearest integer.

Metallic alloy	$T_g^c$ (K)	$m_c$	$T_g^v$ (K)	$m_v$	Reference
<b>Quinary</b>					
Zr <sub>46.75</sub> Ti <sub>8.25</sub> Cu <sub>7.5</sub> Ni <sub>10</sub> Be <sub>27.5</sub>	633	34	596	44	[11]
Zr <sub>41.2</sub> Ti <sub>13.8</sub> Cu <sub>12.5</sub> Ni <sub>10</sub> Be <sub>22.5</sub>	648	39	615	50	[12]
Fe <sub>30.8</sub> Co <sub>46.2</sub> P <sub>14</sub> B <sub>6</sub> Al <sub>3</sub>	724	43			[13]
<b>Quaternary</b>					
Zr <sub>65</sub> Cu <sub>17.5</sub> Ni <sub>10</sub> Al <sub>7.5</sub>	633	35			[14]
Pd <sub>40</sub> Ni <sub>10</sub> Cu <sub>30</sub> P <sub>20</sub>	575	52	502	59	[15]
Ni <sub>75</sub> P <sub>16</sub> B <sub>6</sub> Al <sub>3</sub>	691	53			[13]
<b>Ternary</b>					
Zr <sub>65</sub> Al <sub>7.5</sub> Cu <sub>27.5</sub>	650	35	640	35	[16]
La <sub>55</sub> Al <sub>25</sub> Ni <sub>20</sub>	480	32	462	33	[17] for $\eta$ , [18] for $T_g^c$
Mg <sub>65</sub> Cu <sub>25</sub> Y <sub>10</sub>	420	41	411	45	[19]
Pd <sub>64</sub> Ni <sub>16</sub> P <sub>20</sub>	582	51			[13]
Pd <sub>48</sub> Ni <sub>32</sub> P <sub>20</sub>	582	41	566	48	[20]
Pd <sub>40</sub> Ni <sub>40</sub> P <sub>20</sub>	580	41			[13]
Pd <sub>37.5</sub> Ni <sub>37.5</sub> P <sub>25</sub>	619	51			[13]
Pd <sub>36.5</sub> Ni <sub>36.5</sub> P <sub>27</sub>	635	62			[13]
Pd <sub>16</sub> Ni <sub>64</sub> P <sub>20</sub>	587	50			[13]
Pd <sub>77.5</sub> Cu <sub>6</sub> Si <sub>16.5</sub>	635	52	613	73	[13]
Pd <sub>77</sub> Cu <sub>6.5</sub> Si <sub>16.5</sub>	635	64	620	75	[21]
Pt <sub>64</sub> Ni <sub>16</sub> P <sub>20</sub>	482	50			[13]
Pt <sub>60</sub> Ni <sub>15</sub> P <sub>25</sub>	482	50	463	64	[13]
Pt <sub>60</sub> Ni <sub>15</sub> P <sub>25</sub>	485	66	467	68	[22]
Pt <sub>56</sub> Ni <sub>14</sub> P <sub>30</sub>	498	56			[13]
Pt <sub>45</sub> Ni <sub>30</sub> P <sub>25</sub>	495	42	482	48	[20]
Au <sub>76.9</sub> Ge <sub>13.65</sub> Si <sub>9.45</sub>	295	60	285	85	[23]
Au <sub>76.9</sub> Ge <sub>13.65</sub> Si <sub>9.45</sub>	295	60	286	80	[24]

Most of the ternary metallic alloys in table 1 consist of Pt–Ni–P and Pd–Ni–P systems since these metal–metalloid component alloys were among the earliest alloys found to exhibit a wide supercooled liquid range of  $\approx 50$ – $60$  K between the glass transition and crystallization

temperatures during heating [13, 25]. Due to the high thermal stability of the supercooled liquid phase, these alloys have been studied quite intensively in the past. For the Pd–Cu–Si, Au–Ge–Si and Pt<sub>65</sub>Ni<sub>15</sub>P<sub>25</sub> alloys, the results for  $m_c$  and  $m_v$  estimated from two different sources each are also shown in table 1. The values of  $m_c$  from the different references do not agree very well for the Pd–Cu–Si and Pt<sub>60</sub>Ni<sub>15</sub>P<sub>25</sub> alloys, although they do agree quite well for  $m_v$ . It is unclear whether the discrepancy in  $m_c$  for the same alloy is due to factors such as differences in sample preparation, thermal history before and during measurement, and the method of measurement.

Several deductions can be drawn from table 1. Firstly, considering only  $m_c$ , we see that the group of metallic alloys have values in the range  $32 \leq m_c \leq 66$  with an average of  $m_c = 48$ . This indicates that these alloys lie in the intermediate category according to Angell's classification scheme. The intermediate range spanned by  $m_c$  is weighted more heavily on the side closer to the strong limit compared to the fragile extreme. For example, twelve of the alloys listed have  $m_c \leq 50$  and there are four with  $60 \leq m_c \leq 66$ . (The two different values of  $m_c$  for Pt<sub>60</sub>Ni<sub>15</sub>P<sub>25</sub> have not been included in this count.)

Secondly,  $m_v > m_c$  for all of the alloys for which it has been possible to compute  $m_v$ . This is because  $T_g^v < T_g^c$  and the same fitting parameters for calculating  $m_c$  have been used to estimate  $m_v$  from equation (4) or equation (5). (Note that for Zr<sub>65</sub>Al<sub>7.5</sub>Cu<sub>27.5</sub>,  $m_c = 34.9$  and  $m_v = 35.4$  which round off to the same nearest integer.) Those alloys which are more fragile, i.e. which possess a greater degree of dynamic heterogeneity within the supercooled liquid state, display a greater variation in the temperature dependence of the viscosity and thus a larger difference between  $m_v$  and  $m_c$ . Examples include the Si-containing alloys, Pd–Cu–Si and Au–Ge–Si, which exhibit a relatively large  $\Delta m_{cv} = m_c - m_v$  over a small temperature change  $\Delta T_g = T_g^c - T_g^v$ . Stronger metallic alloys, such as the Zr–Cu-containing ones, display a smaller  $\Delta m_{cv}/\Delta T_g$  ratio.

A third observation is that the five-component alloys lie closer to the strong-liquid side. It has been shown recently that the Zr–Ti–Cu–Ni–Be supercooled liquid is very stable against crystallization with critical cooling rates for glass formation of the order of  $10 \text{ K s}^{-1}$  or less [26, 27]. This has opened the door to the casting of glassy rods and ingots with the smallest dimension extending over several millimetres or more [26], as opposed to conventional thin amorphous ribbons of thickness less than 0.1 mm. Such bulk-forming ability, however, is not restricted to quinary alloys only, as discoveries in the past decade have shown. Examples of these lower-component, bulk metallic glass formers include families of the quaternary Zr–Ni–Cu–Al [14, 28] and the ternary La–Al–Ni [17, 18, 29, 30], Mg–Cu–Y [19, 31, 32] and Zr–Al–Cu [16, 33, 34] alloys which, as can be seen in table 1, are fairly strong liquids. Some of the Pd–Ni–P and Pt–Ni–P systems shown in table 1 also have a relatively small fragility parameter (around 40) but we are unaware of attempts to cast these amorphous alloys in bulk form, except for Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> [35–37].

There appears to be a trend whereby bulk glass-forming metallic alloys which require only low critical cooling rates display relatively small fragility parameters in the range 30–40. Other less thermally stable supercooled metallic liquids are more fragile. Busch, Bakke and Johnson [11] have proposed several reasons to explain why bulk metallic glasses are stronger supercooled liquids. As discussed by these workers, structural studies of these materials indicate that they possess a relatively small amount of free volume and significant chemical short-range ordering in the melt. The low thermal and electrical conductivity of these bulk metallic glasses also suggest that there is a greater degree of localization of electrons in directional bonding. The result is that these alloys are more rigid and thus are stronger metallic glass formers in the sense that the viscous flow changes more gradually with temperature.

### 3. Conclusions

In summary, viscosity data near and below the calorimetric glass transition temperature for 21 multi-component metallic alloys indicate that these materials are intermediate glass formers with an average fragility parameter of approximately 50. Of course, measurements of viscosity or other relaxation time data well into the supercooled liquid region are required for a wider range of metallic glass formers in order to see whether the intermediate fragility strength is a general characteristic of such alloys. Due to the relative simplicity of the structure of metallic alloys, however, they are not expected to be very fragile liquids as is the case for many polymers [5].

More recently there has been extensive research into the production and characterization of bulk amorphous metallic alloys with exceptionally favourable glass-forming ability. Quinary and quaternary alloys appear to be the main members of this subgroup of metallic glass formers. However, a few ternary metallic alloys have also been recently fabricated which fall into this category. It is found that these bulk metallic glass formers exhibit a small fragility index in the range of 30–40. It appears that there might be a general positive correlation between better glass-forming ability and stronger supercooled metallic liquids.

It would be desirable to explore more combinations of the metallic elements in order to design other bulk metallic glasses due to the benefit of lower production costs and the potential of often enhanced properties of the crystalline phase produced from the annealing of amorphous alloys as compared to formation from conventional methods.

### Acknowledgments

I would like to thank Dr An Pang Tsai for bringing several pertinent references to my attention. I am also grateful for a Science and Technology Agency (STA) Fellowship from the Japan Science and Technology Corporation (JST).

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