Exceptionally broad bulk metallic glass formation in the Mg–Cu–Yb system

Karl F. Shamlaye a,*, Kevin J. Laws a, b, Jörg F. Löffler a

a Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland
b School of Materials Science and Engineering, UNSW Australia, Sydney, NSW 2052, Australia

Abstract

This study presents an extensive series of novel bulk metallic glasses (BMGs) which broadly span all three corners of the Mg–Cu–Yb ternary system. Over 30 alloys were synthesized within a wide composition range from (at.%) Mg: 13–55, Cu: 17.5–45.5, and Yb: 9–70. In terms of composition, this ternary system is considered to be one of the broadest for bulk glass formation known - this probably due to the three elements' thermodynamic compatibility and unique combinations of atomic radii, which generate specific, favoured structural topologies. The investigation reports the design method, critical casting size, thermophysical characteristics and mechanical properties of these new BMGs.

Keywords:
Bulk metallic glasses
Glass-forming ability
Predictive structural model

1. Introduction

While the possibility of metallic glass formation from the melt has been known to science for over 50 years [1], in terms of amorphous alloy discovery and development many potential glass-forming systems remain uncharted. With respect to the periodic table, vast expanses of ternary, quaternary and extended multi-component alloy composition space have yet to be explored [2]. This is because fast, efficient and accurate means of probing composition space are beyond the means of basic alloy production techniques. Despite this, amorphous alloy structural modelling and glass-formation prediction techniques have advanced substantially in the last decade, generating many methods ranging from first principles/ab initio [3–6], thermodynamic [7,8] and topological [3–11] models which prove useful to varying degrees.

With the discovery of bulk glass formation in the Mg–Cu–Y ternary system in 1991 [12], numerous Mg-based ternary glass-forming systems which also contain Cu have been discovered. These have mostly been Mg-rich, based on the Mg–Cu–RE systems [13–17] (where RE = Rare Earth = Y, Gd, Nd, Dy, Tb, Er etc.) or the more recent bulk-glass-forming Mg–Cu–Ca ternary system [18]. Essentially, the driving force behind the production of these high Mg or -Ca containing alloys has been to develop a new category of light-metal alloys with high specific strengths in addition to other useful engineering properties [19,20]. Typically these ternary compositions are extended to quaternary or quinary alloys in a piecewise manner to enhance glass-forming ability (GFA) and/or other specific properties. For example, 8.5 at.% Ag can be substituted for Cu in the Mg58.5Cu30.5Gd11 alloy (casting thickness, \(D_c = 9 \text{ mm}\)) to obtain a 27 mm bulk glass [21].

However, in terms of amorphous alloy discovery related to this work, Wang and co-workers [22] synthesised amorphous alloys based on the popular Mg65Cu35RE10 formula, with nearly all the Lanthanide series elements, including Yb. In spite of successes with the other RE elements, the XRD trace of a 1 mm diameter Mg65Cu25Yb10 rod specimen showed numerous crystalline peaks. Tsarkov and co-workers [23] also recently investigated the effect of glass forming ability (GFA) by adding Ag and Ca to a Mg65Cu25Yb10 base alloy, which in neither case produced a bulk glass. In light of this it would seem that Yb is not suitable for glass formation within this specific Mg-rich composition space, or at least that it behaves very differently to other Lanthanide elements at this composition.

Cu-based BMGs have generated considerable interest due to their relatively low material cost, notably high compressive fracture strengths (1900–2500 MPa [24,25]) and large plastic strain before fracture (in some cases up to 18%) [26]. However, most have been based on alloy systems that contain at least one group IV transition metal (Zr, Hf and Ti) as a major alloying element, making Cu-based BMGs which do not contain these elements somewhat unique. As an alternative numerous Cu-base BMGs have been recently...
discovered in the Cu–Mg–Ca system [27].

To date the only Yb-based BMGs were found by Wang et al. [28] in the Yb–Zn–Mg system, exhibiting casting diameters of up to 2 mm, which upon minor Cu-addition (5 at.%) increases to a maximum of 4 mm. This suggests a possible window of opportunity for favourable glass formation between Yb, Mg and Cu.

In this work we apply a predictive topological model [10,29] to establish regions of possible glass formation in the Mg–Cu–Yb system. Implementing this method has previously proved useful for discovering numerous novel bulk metallic glasses in a wide range of ternary systems [18,27,29–32]. It is of fundamental scientific interest to ascertain the existence of other simple ternary BMG-forming systems (in particular Mg-, Cu- and Yb-based) and further develop the means by which new systems might be predicted to aid new rapid amorphous alloy development strategies.

2. Alloy design concept

It is mentioned above that Yb appears to behave differently from other lanthanide series metals with respect to glass formation. On careful inspection it is found that Yb stands out among the other lanthanide series metals with respect to glass formation. On this basis it is possible to develop the means by which new systems might be predicted to aid new rapid amorphous alloy development strategies.

It is well known that diffusion kinetics play a key role in the nucleation of crystallites or the retention of the amorphous state upon cooling/relaxation. It is also known that a tightly or efficiently-packed liquid structure significantly impedes atomic diffusion upon cooling from the melt (extrinsically viewed as increased melt viscosity), hindering nucleation kinetics – in turn leading to a lower critical cooling rate and greater glass-forming ability [9,29]. The topological model used in this work to guide us in determining glass-forming composition ranges takes into account the efficiency of packing atoms (considered here to be hard spheres) that constitute the composition of the alloy around each individual atom centre. That is, in a perfectly efficient packing composition every atom in a given atom’s first coordination shell is touching that central atom and its nearest neighbours – that ‘cluster’ of atoms is equivalent to the composition of the alloy. Atomic radii of Cu = 126 p.m., Mg = 160 p.m. and Yb = 194 p.m. were used for this calculation (an in depth description on carrying out these calculations can be found in Refs. [10] and [29]). When each individual atomic centre can be simultaneously efficiently packed at a given alloy composition, the ‘global’ structure of the alloy is considered efficiently packed, and hence most likely to exhibit enhanced glass-forming ability [10]. Mathematically, a larger difference in atomic radii in a ternary system gives a larger range of possible coordination numbers as composition changes throughout the system [29,32]. This means that with a change in alloy composition, atoms in the first coordination shell of a cluster are substituted – the greater the difference in atomic size of constituents, the more significant the progressive change in coordination number. Hence with approximately 20% difference in atomic size between Cu–Mg and Mg–Yb a broad glass-forming range would be expected, similar to that of the Mg–Cu–Ca system [18,29,34].

The 3 heavy black dashed lines in Fig. 1(a) indicate the ideal compositions for perfect packing for all three atomic centres (determined by Laws et al. in Table S1 of reference [10]), applied to the atomic radius ratios of the Mg–Cu–Yb system; these have been shown to be preferred coordination combinations for glass formation [10,36,37]. The coordination number of each element along these perfect packing lines is indicated in <parentheses>. For example, 〈9〉<12〉<15〉 represents a coordination number of 9 around the smallest atom, Cu; 12 around the mid-sized atom, Mg; and 15 around the largest atom, Yb. The yellow-shaded region highlights ±3% deviation from the ideal radius ratio required for perfect packing efficiency, which is considered to be a reasonable fluctuation for bulk glass formation or the possible error in using fixed radii for atoms in a hard-sphere model [10]. These composition regions are also truncated where a complete Cu, Mg or Yb atomic centred cluster cannot be constructed, e.g. a Yb-centred cluster coordinated by 17 atoms cannot be a structural representative of the alloy composition when the Yb content is less than 1/17 + 1 or 5.55 at. %. [10]. From within these calculated regions potential glass-forming compositions from the Mg-, Cu- and Yb-based regions of the Mg–Cu–Yb ternary system were synthesised and analysed.

3. Experimental procedures

The predicted glass-forming compositions were prepared and tested for GFA. Nominal alloy compositions (shown in Tables 1–3) were prepared using high-purity metals; Mg (99.99 wt%), Cu (99.99 wt%), Yb (99.99 wt%). The metals were alloyed in graphite crucibles using an induction furnace in an argon-purged (99.997 wt %) atmosphere. The alloys were tilt cast into a wedge-shaped (10:1 taper) copper mould at temperatures of approximately 100 °C–150 °C above their liquidus to determine their critical casting thicknesses (Zc). For larger glass-forming compositions samples were suction cast in various diameters in 0.5 mm increments to determine their critical casting diameters (Dc). Compression specimens 1.7 mm in diameter were fabricated by suction casting into a cylindrical copper mould, and the ends polished flat and parallel down to a SiC paper 1200 grit finish. The glassy structure was verified using X-ray diffraction (XRD) with a Phillips MRD instrument fitted with a 0.5 mm microcapillary tube and Cu Kα radiation source. Thermophysical data was determined by differential scanning calorimetry (DSC) using a Mettler Toledo DSC1/1700 calorimeter at a heating rate of 20 °C/min. Vickers hardness testing was performed on selected alloys, using a Wolpert MXT-α microhardness tester, with a load of 500 g for 15 s over 20 indents. Compression tests were performed at a strain rate of 1 × 10⁻⁴ s⁻¹ using a Schenck screw-driven mechanical testing machine for up to 5 specimens per selected alloy.

4. Results & discussion

4.1. Glass formation in the Mg-Cu-Yb ternary system

Fig. 1(a) and (b) shows the composition range of the newly discovered bulk glass-forming alloys. Based on the DSC data generated in this work, reported phases and liquidus temperatures
found in binary phase diagrams [38–40], and the similar Cu-Ca-Mg ternary system [41], a liquidus iso-surface of Mg–Cu–Yb ternary system was also generated. It can be seen clearly that the Mg–Cu–Yb ternary system can now be perceived as one of the broadest ternary systems for glass formation, akin to the Mg–Cu–Ca system, where bulk glass formation also occurs in each of the three element-based regions, including an equiatomic element content BMG-forming composition.

Traditionally, bulk metallic glass formation compositions have been associated with the proximity of deep eutectic reactions with exceptionally lowered liquidus temperatures compared to surrounding composition space and very narrow freezing ranges. Such alloys physically require less heat to be drawn by a copper mould, hence faster cooling and a higher perceived critical casting size. The stability of a glass has historically been measured or compared by its thermophysical properties, which traditionally include the reduced glass transition temperature (\(T_g\)) divided by the liquidus temperature, \(T_l\), which for good glass formers tends to be around 0.6. Similarly, the gamma (\(\gamma\)) introduced by Lu and Liu equivalent to the crystallisation temperature \((T_X)\) divided by \((T_g + T_l)\) which approached 0.5 for strong glass-formers [43]. In the Yb-based region, glass formation occurs in close proximity to the ternary eutectic reaction between the Yb solid solution, MgYb and CuYb. However, majority of bulk glass forming compositions with high GFA were found to lie in the Mg- and Cu-based regions in proximity to the liquidus lines/troughs between the Cu2Mg, Mg2Cu and Mg2Yb liquidus phase fields. The largest glass produced in the Mg–Cu–Yb system was the Mg0.4xCu36.36Yb22.9 alloy with critical casting diameter \(D_C = 3.5 \text{ mm}\) which appears to lie directly on a ternary peritectic reaction, between these three specific phases. This indicates that bulk glasses may be formed far from ternary eutectic reactions, which has also only recently been seen in BMG-forming systems [18,29,30]. Coincidently, no bulk glasses are formed in proximity to the Mg-rich and Cu-rich eutectic reactions. These results somewhat contradict classic ideas about metallic glass formation, and the general usefulness of glass forming indicators, suggesting other aspects may have significant effect on glass-forming ability.

We show that there is good agreement between bulk glass formation and the simultaneously efficiently-packed composition regions highlighted in yellow in Fig. 1(a) and glasses tend to increase in critical casting size when closer to the ideal packing lines (black dashed lines) and liquidus phenomena such as liquidus lines. It is also worth noting that the majority of bulk glasses occur towards the centre of the ternary diagrams where chemical entropy is highest.

It should also be pointed out that in all cases the critical casting thickness \((Z_C)\) determined by wedge casting is smaller than or equal to the critical casting diameter \((D_C)\). This follows the trend observed

Table 1

Critical casting thickness and thermophysical properties of Mg-based BMGs in the Mg–Cu–Yb system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(Z_C) (mm)</th>
<th>(D_C) (mm)</th>
<th>(T_g) (°C)</th>
<th>(T_X) (°C)</th>
<th>(\Delta T) (°C)</th>
<th>(T_m) (°C)</th>
<th>(T_l) (°C)</th>
<th>(T_g/T_l)</th>
<th>(\gamma)</th>
<th>HV0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg87.5Cu36Yb9</td>
<td>1.4</td>
<td>2.0</td>
<td>95</td>
<td>125</td>
<td>30</td>
<td>398</td>
<td>488</td>
<td>0.484</td>
<td>0.353</td>
<td>217 ± 1.7</td>
</tr>
<tr>
<td>Mg85.4Cu34.3Yb14.2</td>
<td>0.9</td>
<td>1.0</td>
<td>115</td>
<td>133</td>
<td>18</td>
<td>348</td>
<td>496</td>
<td>0.505</td>
<td>0.351</td>
<td>195 ± 6.0</td>
</tr>
<tr>
<td>Mg80Cu30Yb10</td>
<td>1.9</td>
<td>2.5</td>
<td>119</td>
<td>138</td>
<td>19</td>
<td>391</td>
<td>484</td>
<td>0.518</td>
<td>0.358</td>
<td>263 ± 3.4</td>
</tr>
<tr>
<td>Mg75Cu25Yb25</td>
<td>1.1</td>
<td>1.5</td>
<td>114</td>
<td>132</td>
<td>18</td>
<td>439</td>
<td>485</td>
<td>0.511</td>
<td>0.354</td>
<td>230 ± 4.0</td>
</tr>
<tr>
<td>Mg70Cu30Yb30</td>
<td>1.1</td>
<td>1.5</td>
<td>118</td>
<td>135</td>
<td>28</td>
<td>444</td>
<td>580</td>
<td>0.461</td>
<td>0.337</td>
<td>247 ± 4.9</td>
</tr>
<tr>
<td>Mg65Cu35Yb30</td>
<td>1.6</td>
<td>2.0</td>
<td>120</td>
<td>147</td>
<td>27</td>
<td>442</td>
<td>584</td>
<td>0.459</td>
<td>0.336</td>
<td>236 ± 3.4</td>
</tr>
<tr>
<td>Mg60Cu40Yb20</td>
<td>1.7</td>
<td>2.0</td>
<td>120</td>
<td>147</td>
<td>27</td>
<td>443</td>
<td>584</td>
<td>0.459</td>
<td>0.336</td>
<td>236 ± 3.4</td>
</tr>
<tr>
<td>Mg55Cu45Yb15</td>
<td>2.5</td>
<td>3.5</td>
<td>117</td>
<td>138</td>
<td>21</td>
<td>392</td>
<td>483</td>
<td>0.516</td>
<td>0.359</td>
<td>235 ± 6.3</td>
</tr>
<tr>
<td>Mg50Cu50Yb15</td>
<td>2.2</td>
<td>3.0</td>
<td>116</td>
<td>140</td>
<td>24</td>
<td>424</td>
<td>503</td>
<td>0.501</td>
<td>0.355</td>
<td>223 ± 6.1</td>
</tr>
<tr>
<td>Mg45Cu55Yb15</td>
<td>2.0</td>
<td>2.5</td>
<td>118</td>
<td>139</td>
<td>21</td>
<td>419</td>
<td>502</td>
<td>0.505</td>
<td>0.353</td>
<td>219 ± 4.5</td>
</tr>
</tbody>
</table>

* \(T_g\) values quoted herein are the onset temperature of the glass transition.
in other systems where both $Z_c$ and $D_c$ have been determined for the same alloy [18,29–32] and correlates with the geometric heat transfer relation, whereby $Z_c = 0.7D_c$ [44]. Here the physical resolution in determining $D_c$ is limited compared to $Z_c$ by the incremental 0.5 mm diameter step size of our cylindrical moulds.

Examining the as-cast wedges, it was observed that certain alloys showed no effects of shrinkage cracking due to thermal contraction associated with cooling and crystallisation (i.e. stayed as a single wedge, with no cracks caused by thermal stress effects upon being cast); hence, these alloys were considered structurally relatively stable and were selected for compression testing.

4.2. Mg-based BMGs

Table 1 gives the critical casting thickness and diameter of the Mg-base glass forming alloys, along with their thermophysical properties and Vickers hardness where appropriate. The GFA appears to increase with increasing amounts of Cu, and decreasing concentrations of Yb — for a given Mg concentration. The average $D_c$ for these alloys is 2.0 mm and interestingly, only 3 compositions (Mg50Cu36.4Yb3.6, Mg40.8Cu36.4Yb22.9, and Mg36.4Cu27.3Yb36.4) show as good or better GFA than the equi-atomic composition. Fig. 2 shows the differential scanning calorimetry (DSC) profiles of selected Mg-based BMGs. A clear glass transition ($T_g$) and subsequent crystallisation reaction can be seen in each instance, with considerable relaxation events (beta relaxation) prior to $T_g$ evident in most compositions, as also seen in other Mg-Cu BMG alloys [45]. These Mg-based BMGs exhibit glass transition and crystallisation temperatures considerably lower than those of other Mg-Cu-RE BMGs, and are again more closely akin to the Mg–Cu–Ca [18] or even Mg–Zn–Ca [46] BMGs. Of particular note, the Mg55Cu36Yb9 BMG has a very low $T_g$ of 95 °C, but nonetheless this alloy has the largest supercooled liquid region (SCLR), $\Delta T_x (=T_x - T_g)$ of 30 °C, of all the Mg-based BMGs, indicating the best processing window available for thermoplastic forming. Relative to the glass forming indicators $T_g$ and $\gamma$, Mg-based alloys here exhibit quite low values compared to other glass-forming systems. This is likely due to the fact that these are not eutectic compositions and the melting reactions observed span temperature intervals from 41 to 148 °C, with the Mg2Cu phase playing a dominant role in the final melting point of these alloys. However, the largest glass formers do indeed exhibit the larger values of $T_g$ and $\gamma$.

It is quite clear in Fig. 1 that glass formation avoids higher liquidus temperature regions in closer proximity to high melting point binary intermetallics such as Mg2Cu and Mg2Yb. Despite having good packing efficiency, it is also apparent that bulk glasses are not formed in close proximity to the saddle-point between Mg2Cu and Mg2Yb close to the popular Mg50Cu25RE10 composition space (a similar result can be observed in the Mg–Cu–Ca system). It is noted that in other trivalent rare earth binary systems such as Mg–Y, Mg–Gd and Mg–Nd the congruent solidification reaction observed for Mg2Yb and Mg2Ca does not exist; rather, a series of peritectic reactions occur with a range of other Mg-rich Mg–RE intermetallics. This is a result of the specific electronic and topological differences between Yb and other RE elements, which is the likely reason that previous researchers were unable to obtain a bulk glass for the Mg55Cu25Yb10 composition [20,23]. Broadly speaking, the maximum GFA/$D_c$ of the Mg–Cu–Yb BMGs studied here are not as large as those found in the similar Mg–Cu–Ca system (e.g. Mg55Cu36.4Yb9 has a $D_c = 5$ mm).

Table 1 gives the critical casting thickness and diameter of the Mg-base glass forming alloys, along with their thermophysical properties and Vickers hardness where appropriate. The GFA appears to increase with increasing amounts of Cu, and decreasing concentrations of Yb — for a given Mg concentration. The average $D_c$ for these alloys is 2.0 mm and interestingly, only 3 compositions (Mg50Cu36.4Yb3.6, Mg40.8Cu36.4Yb22.9, and Mg36.4Cu27.3Yb36.4) show as good or better GFA than the equi-atomic composition. Fig. 2 shows the differential scanning calorimetry (DSC) profiles of selected Mg-based BMGs. A clear glass transition ($T_g$) and subsequent crystallisation reaction can be seen in each instance, with considerable relaxation events (beta relaxation) prior to $T_g$ evident in most compositions, as also seen in other Mg-Cu BMG alloys [45]. These Mg-based BMGs exhibit glass transition and crystallisation temperatures considerably lower than those of other Mg-Cu-RE BMGs, and are again more closely akin to the Mg–Cu–Ca [18] or even Mg–Zn–Ca [46] BMGs. Of particular note, the Mg55Cu36Yb9 BMG has a very low $T_g$ of 95 °C, but nonetheless this alloy has the largest supercooled liquid region (SCLR), $\Delta T_x (=T_x - T_g)$ of 30 °C, of all the Mg-based BMGs, indicating the best processing window available for thermoplastic forming. Relative to the glass forming indicators $T_g$ and $\gamma$, Mg-based alloys here exhibit quite low values compared to other glass-forming systems. This is likely due to the fact that these are not eutectic compositions and the melting reactions observed span temperature intervals from 41 to 148 °C, with the Mg2Cu phase playing a dominant role in the final melting point of these alloys. However, the largest glass formers do indeed exhibit the larger values of $T_g$ and $\gamma$.

It is quite clear in Fig. 1 that glass formation avoids higher liquidus temperature regions in closer proximity to high melting point binary intermetallics such as Mg2Cu and Mg2Yb. Despite having good packing efficiency, it is also apparent that bulk glasses are not formed in close proximity to the saddle-point between Mg2Cu and Mg2Yb close to the popular Mg50Cu25RE10 composition space (a similar result can be observed in the Mg–Cu–Ca system). It is noted that in other trivalent rare earth binary systems such as Mg–Y, Mg–Gd and Mg–Nd the congruent solidification reaction observed for Mg2Yb and Mg2Ca does not exist; rather, a series of peritectic reactions occur with a range of other Mg-rich Mg–RE intermetallics. This is a result of the specific electronic and topological differences between Yb and other RE elements, which is the likely reason that previous researchers were unable to obtain a bulk glass for the Mg55Cu25Yb10 composition [20,23]. Broadly speaking, the maximum GFA/$D_c$ of the Mg–Cu–Yb BMGs studied here are not as large as those found in the similar Mg–Cu–Ca system (e.g. Mg55Cu36.4Yb9 has a $D_c = 5$ mm).

Fig. 2(a) shows the differential scanning calorimetry (DSC) traces of Mg-based metallic glasses in the Mg–Cu–Yb system.

Fig. 2(b) shows the X-ray diffraction (XRD) spectra of selected Mg-based glasses in the Mg–Cu–Yb system.
Mg-based BMGs, indicating the characteristic diffuse halo of an amorphous microstructure at the centre section for the sample diameters indicated.

### 4.3. Cu-based BMGs

Table 2 presents the critical casting thickness and associated casting diameter, thermophysical properties and Vickers hardness of the Cu-based BMGs. The GFA of these alloys appears to reach a maximum when the Cu concentration is 36–45 at.% and the Mg concentration is 31–36 at.%; however, GFA diminishes quickly with increasing Yb content. Fig. 3(a) shows the DSC profiles of selected Cu-based BMGs. The alloys have glass stability similar to that of the Mg-based compositions, as shown by the narrow SCLR range between 15 and 29 °C, with \( \Delta T_{\text{g-average}} = 23.3 \) °C. The alloy Cu45.5Mg36.4Yb18.1 exhibits as good a \( \Delta T_x \) (29 °C), similar to the best Mg-based BMG. A general trend is seen for fixed Cu concentrations (45 at.%, 40 at.% and 36 at.%), where \( T_g \) and \( T_x \) increase with a decrease in Mg and an increase in Yb content (conversely the casting thickness increases with increasing Mg/decreasing Yb). Two compositions, Cu40.9Mg36.4Yb22.7 and Cu36.4Mg36.4Yb27.2, have low freezing ranges (60 °C and 27 °C, respectively) and both show a relatively narrow, single endothermic peak during melting, which indicates their proximity to the local peritectic reaction and liquidus lines between the CuMg and MgCu or Mg2Yb liquidus phase fields. Cu40.9Mg36.4Yb22.7 is one of the best Cu-based glass formers, along with Cu45.5Mg36.4Yb18.1, Cu40.9Mg31.8Yb17.3 and Cu36.4Mg36.4Yb27.2 (all with a \( D_t \) of 3 mm); these however, have large melting ranges of 118 °C, 157 °C, and 122 °C respectively.

Relative to the GFA indicators \( T_g \) and \( \gamma \), these Cu-based alloys also exhibit quite low values compared to other glass-forming systems, again due to their large distance from the local eutectic reactions. The correlation between critical casting size, \( T_g \) and \( \gamma \) is quite poor in this region. Where the Cu40.9Mg36.4Yb22.7 alloy with the highest values of \( T_g \) and \( \gamma \) exhibits only marginal glass formation of 1 mm critical casting size, whereas the Cu45.5Mg36.4Yb18.1, Cu40.9Mg36.4Yb22.7, Cu40.9Mg31.8Yb17.3 and Cu36.4Mg36.4Yb27.2 alloys, all with critical casting diameters of 3 mm exhibit considerably lower values of \( T_g \) and \( \gamma \). This is an interesting observation, where liquidus temperature is decreasing with increasing Yb content as compositions continue down a liquidus trough, however GFA is also decreasing, even in close proximity to the efficient packing lines. This is thought to be a result of the specific crystallites being nucleated, whereby the larger glass-formers in this region lie well within the CuMg liquidus phase field, where a small fraction of this higher melting point phase appears to increase the final liquidus temperatures of these particular alloys. Surprisingly, this does not seem to harm their glass-forming ability. However, glass forming ability drops sharply when approaching the Cu2Yb and Cu7Yb liquidus phase fields, e.g. GFA drops to only 1 mm at the Cu40.4Mg27.3Yb31.8 composition. This indicates that the nucleation

<table>
<thead>
<tr>
<th>Composition</th>
<th>( Z_c ) (mm)</th>
<th>( D_t ) (mm)</th>
<th>( T_g ) (°C)</th>
<th>( \Delta T_g ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( T_l ) (°C)</th>
<th>( T_{\text{g-average}} ) (°C)</th>
<th>( \gamma )</th>
<th>HV0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu45.5Mg36.4Yb18.1</td>
<td>2.4</td>
<td>3.0</td>
<td>110</td>
<td>139</td>
<td>29</td>
<td>437</td>
<td>640</td>
<td>0.419</td>
<td>0.318</td>
</tr>
<tr>
<td>Cu45.5Mg36.4Yb22.7</td>
<td>1.8</td>
<td>2.5</td>
<td>117</td>
<td>145</td>
<td>28</td>
<td>404</td>
<td>630</td>
<td>0.432</td>
<td>0.323</td>
</tr>
<tr>
<td>Cu40.9Mg36.4Yb22.7</td>
<td>0.8</td>
<td>1.0</td>
<td>127</td>
<td>152</td>
<td>25</td>
<td>375</td>
<td>607</td>
<td>0.455</td>
<td>0.332</td>
</tr>
<tr>
<td>Cu36.4Mg36.4Yb27.2</td>
<td>1.2</td>
<td>3.0</td>
<td>112</td>
<td>139</td>
<td>27</td>
<td>447</td>
<td>663</td>
<td>0.411</td>
<td>0.312</td>
</tr>
<tr>
<td>Cu40.9Mg31.8Yb17.3</td>
<td>0.8</td>
<td>1.0</td>
<td>127</td>
<td>152</td>
<td>25</td>
<td>375</td>
<td>607</td>
<td>0.455</td>
<td>0.332</td>
</tr>
<tr>
<td>Cu40.9Mg31.8Yb27.3</td>
<td>0.8</td>
<td>1.0</td>
<td>127</td>
<td>152</td>
<td>25</td>
<td>375</td>
<td>607</td>
<td>0.455</td>
<td>0.332</td>
</tr>
<tr>
<td>Cu40.4Mg27.3Yb31.8</td>
<td>0.7</td>
<td>1.0</td>
<td>139</td>
<td>154</td>
<td>15</td>
<td>358</td>
<td>604</td>
<td>0.470</td>
<td>0.331</td>
</tr>
<tr>
<td>Cu36.4Mg36.4Yb27.2</td>
<td>2.2</td>
<td>3.0</td>
<td>117</td>
<td>141</td>
<td>24</td>
<td>434</td>
<td>556</td>
<td>0.470</td>
<td>0.340</td>
</tr>
<tr>
<td>Cu36.4Mg31.8Yb17.3</td>
<td>1.3</td>
<td>1.5</td>
<td>123</td>
<td>143</td>
<td>20</td>
<td>418</td>
<td>573</td>
<td>0.468</td>
<td>0.335</td>
</tr>
<tr>
<td>Cu36.4Mg31.8Yb27.3</td>
<td>0.8</td>
<td>1.0</td>
<td>133</td>
<td>156</td>
<td>23</td>
<td>443</td>
<td>470</td>
<td>0.546</td>
<td>0.373</td>
</tr>
</tbody>
</table>

\( a \) \( T_g \) values quoted herein are the onset temperature of the glass transition.
and growth kinetics of the Cu2Yb and Cu2Yb phases is likely much higher, hence the lower GFA of these alloys. These glasses belong to the <10>⟨14⟩⟨17⟩ topological family and generally exhibit a higher GFA when in close proximity to the ideal packing efficiency line in Fig. 1(a) with the exception of when approaching the Cu2Yb and Cu2Yb liquidus phase fields. This exemplifies the role of kinetics again with respect to packing efficiency, where the largest glasses in the region are some distance from liquidus lines and have large solidification intervals and also the role of nucleation kinetics the competing crystalline phases, whereby the Cu2Mg phase appears to be much more sluggish than Cu2Yb and Cu2Yb. Again, these Cu-based Cu–Mg–Yb glasses exhibit a somewhat lower GFA than Cu–Mg–Ca BMGs, e.g., Cu36Mg31Ca31.8, Dc = 8 mm [29] compared to Cu36Mg31.8Yb1.8 where Dc = 1.5 mm. Fig. 3(b) shows the XRD spectra of selected Cu-based BMGs, indicating the glassy structure of the alloys.

4.4. Yb-based BMGs

Table 3 gives the critical casting thickness and diameter of the Yb-base metallic glasses, their thermophysical properties and their Vickers hardness. The Yb-based region produces BMGs at a higher solvent concentration range (33.3–70 at. % Yb) than the Mg- and Cu-based regions. While the largest BMG found here had a maximum Dc of 2.5 mm, for Yb90Mg20Cu20 further refinement could possibly yield glasses comparable to the Mg- and Cu-based regions in this system. The number of ternary Yb-based BMGs is much smaller than the Mg-based compositions and much smaller than the Ca-based BMGs, indicating the glassy structure of the alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Zc (mm)</th>
<th>Dc (mm)</th>
<th>Tg (°C)</th>
<th>Tx (°C)</th>
<th>(\Delta T_g) (°C)</th>
<th>Tm (°C)</th>
<th>Tl (°C)</th>
<th>(\gamma)</th>
<th>HV0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb90Mg20Cu0</td>
<td>0.6</td>
<td>–</td>
<td>136</td>
<td>155</td>
<td>19</td>
<td>443</td>
<td>472</td>
<td>0.549</td>
<td>0.371</td>
</tr>
<tr>
<td>Yb90Mg21.7Cu17.5</td>
<td>1.2</td>
<td>1.5</td>
<td>122</td>
<td>142</td>
<td>20</td>
<td>417</td>
<td>457</td>
<td>0.541</td>
<td>0.369</td>
</tr>
<tr>
<td>Yb90Mg20Cu0</td>
<td>1.9</td>
<td>2.5</td>
<td>140</td>
<td>158</td>
<td>18</td>
<td>412</td>
<td>438</td>
<td>0.581</td>
<td>0.383</td>
</tr>
<tr>
<td>Yb80Mg31Cu5</td>
<td>0.7</td>
<td>1.0</td>
<td>144</td>
<td>160</td>
<td>16</td>
<td>411</td>
<td>468</td>
<td>0.563</td>
<td>0.374</td>
</tr>
<tr>
<td>Yb70Mg26Cu7</td>
<td>1.0</td>
<td>1.0</td>
<td>138</td>
<td>156</td>
<td>20</td>
<td>404</td>
<td>468</td>
<td>0.555</td>
<td>0.374</td>
</tr>
<tr>
<td>Yb60Mg33Cu7</td>
<td>1.2</td>
<td>1.5</td>
<td>136</td>
<td>153</td>
<td>17</td>
<td>406</td>
<td>474</td>
<td>0.548</td>
<td>0.369</td>
</tr>
<tr>
<td>Yb60Mg25Cu5</td>
<td>1.3</td>
<td>1.5</td>
<td>146</td>
<td>161</td>
<td>15</td>
<td>413</td>
<td>475</td>
<td>0.560</td>
<td>0.372</td>
</tr>
<tr>
<td>Yb50Mg30Cu10</td>
<td>0.8</td>
<td>1.0</td>
<td>151</td>
<td>160</td>
<td>16</td>
<td>407</td>
<td>464</td>
<td>0.575</td>
<td>0.378</td>
</tr>
<tr>
<td>Yb60Mg20Cu20</td>
<td>0.6</td>
<td>–</td>
<td>151</td>
<td>168</td>
<td>17</td>
<td>433</td>
<td>477</td>
<td>0.565</td>
<td>0.376</td>
</tr>
<tr>
<td>Yb60Mg20Cu10</td>
<td>0.8</td>
<td>1.0</td>
<td>142</td>
<td>161</td>
<td>19</td>
<td>438</td>
<td>462</td>
<td>0.565</td>
<td>0.377</td>
</tr>
</tbody>
</table>

4.5. Mechanical properties

Fig. 5 shows an average contour plot of the variation in Vickers hardness over the glass forming range. Associated errors are included in Tables 1–3. It can be clearly seen that as the Yb-content is increased the BMGs become softer. Despite local minor fluctuations in hardness, one interesting result is a local ‘hard region’ located in close proximity to the Cu36Mg31.8Yb1.8 composition, and a ‘soft trough’ extending below this into a more copper-rich composition space. Similar fluctuations were observed by Laws et al. in the Cu-based region of the Ca–Cu–Mg ternary system in
comparable composition ranges if Ca is exchanged for Yb [29]. These fluctuations were found to correspond to fluctuations in alloy density, where a higher density resulted in higher alloy hardness. This was attributed to local structural packing efficiency and the possibility of medium range order between specific atomic clusters (in that particular case Cu-centred clusters). It is also possible that this local hard region and soft trough could correspond to the structural transition from the $<10><13><17>$ topology to the $<10><14><17>$ topology as both Cu and Mg are increased. This indicates that hardness (or strength) in these BMGs may not be dictated purely by systematic changes in chemistry, and that local structure plays an important role.

Fig. 6 shows stress-strain curves of selected alloys tested in uniaxial compression. Several alloy compositions which appeared more resistant to fracture during handling were selected for compression testing. It was found that the equiatomic Mg$_{33.4}$Cu$_{33.3}$Yb$_{33.3}$ BMG composition displays a fracture strength ($\sigma_f$) of 455 MPa. In comparison, lowering the Cu content slightly (with equal increases in Mg and Yb content) to Mg$_{36.36}$Cu$_{27.27}$Yb$_{36.36}$ gives a slight increase in strength of 488 MPa. A similar composition shift to lower Yb content in the Cu$_{36.4}$Mg$_{36.4}$Yb$_{27.2}$ BMG results in a significant strength increase to $\sigma_f = 558$ MPa. The alloy with the highest GFA found, Mg$_{40.8}$Cu$_{36.4}$Yb$_{22.9}$, displays the highest fracture strength of alloys tested at 612 MPa; the composition also has the maximum possible Cu content (36 at.%) for bulk glass formation. Conversely, the largest GFA Yb-based composition, Yb$_{60}$Mg$_{20}$Cu$_{20}$, displays the lowest strength value of the alloys tested, at $\sigma_f = 418$ MPa. Typically, the selected compositions exhibit the usual elasticity range for BMGs, between 1.5 and 2%. These strength values tend to correlate with the hardness profile of the system, and fracture strength is...
generally 2.5–3 times the hardness value [46].

Relatively speaking, these BMGs exhibit low fracture strengths when compared to most Mg-based BMGs or the Ca–Cu–Mg BMGs in both the Cu-based and Ca-based regions. The general lower hardness of Yb-alloys can be attributed to elastic correlations of elemental Ytterbium. As noted by Wang et al. [28], Yb-based Yb–Zn–Mg (–Cu) BMGs have generally low mechanical properties, such as low elastic modulus, Poisson’s ratio and Vickers hardness — an occurrence which is also exhibited by these new Yb-based BMGs. On the other hand, increasing the amount of Cu relative to the Yb content generally leads to increased hardness. This may be due to the increase in the number of Cu–Yb pairs, which possess the highest negative heat of mixing among the atom pairs present in the system.

5. Concluding summary

An ensemble of Mg-based, Cu-based, and Yb-based BMG-forming alloys was discovered over a broad composition range using a topological efficient atomic packing model [10]. The maximum critical casting diameter found within the system was 3.5 mm for the Mg-based Mg70Cu25Er10 and Mg-based Mg50Cu25Yb25 alloy. However, several Cu-based compositions had a critical casting diameter of 3 mm and the Cu-based glasses exhibited higher GFA over a broader composition range. With regard to GFA, further improvements in critical casting size may be possible in this system through composition optimisation.

With respect to classic glass-forming indicators, such as $T_g$ and $\gamma$, these alloys only loosely follow trends of glass forming tendency, where these values for the Yb-based BMGs indicate a high glass forming tendency, their critical casting sizes were generally considerably smaller than those of the Mg- and Cu-based BMGs which exhibited much lower values of $T_g$ and $\gamma$. This is largely owing to the compositional distance of the Mg- and Cu-based BMGs from deep eutectic reactions and their broad solidus-liquidus intervals. Glass formation and glass-forming ability was also found to be highly dependent on the corresponding liquidus phase fields within which the alloys lie, whereby those in the Cu2Mg liquidus phase field exhibited the highest GFA which quickly diminishes as compositions approach the Cu4Yb and Cu2Yb liquidus phase fields.

The Mg- and Cu-based glasses were determined to belong to the $<10> <13> <17>$ and $<10> <14> <17>$ topological families, forming glasses in this pre-determined composition space. The Yb-based BMGs were found to show lower glass forming sizes, forming BMGs in the $<9> <12> <15>$ topological composition space. Glass-forming ability tended to increase as compositions approached the ideal topological atomic packing conditions (ideal packing efficiency lines) in this alloy system. These results highlight the effectiveness of using topological models to predict glass-forming compositions, particularly in unexplored systems where no or inconclusive ternary phase diagrams exist.

While it has been demonstrated that in terms of GFA, Yb is a viable topological substitute for Ca in the Mg–Cu–Ca ternary system, further investigation or modelling could be used to explain the lesser glass-forming ability of the Mg–Cu–Yb ternary system. It is also anticipated that multi-component systems beyond this ternary such as Mg–Cu–Ag–Yb, Mg–Cu–Zn–Yb and Mg–Cu–Ni–Yb will likely yield BMGs, which are currently being synthesised by our research group.

Acknowledgements

This work was supported by the Swiss National Science Foundation (SNF Grant No. 200020-153103) and the Australian Research Council (Grant No. DE120102588).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.actamat.2017.02.013.

References

[31] K.J. Laws, J.D. Cao, C. Reddy, K.F. Shamlaye, B. Gun, M. Ferry, Ultra-magnesium-


