Alloy design strategies for sustained ductility in Mg-based amorphous alloys — Tackling structural relaxation

K.J. Laws a, b, D. Granata a, J.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, Sydney, NSW 2052, Australia

ARTICLE INFO

Article history:
Received 14 July 2015
Accepted 31 August 2015
Available online xxx

Keywords:
Metallic glasses
Amorphous alloys
Magnesium
Structural relaxation
Crystallization
Thermodynamics
Mechanical properties
Differential scanning calorimetry

ABSTRACT

Mg-based metallic glasses are promising candidates for use in light-weight, high-specific-strength applications, but their low fracture toughness and rapid room-temperature structural relaxation have so far prevented their deployment. In this study we present various design strategies for tackling structural relaxation via studying several Mg-based amorphous alloy systems during room-temperature aging. Our investigations show that relaxation kinetics is strongly affected by solute content, solute type and glass transition temperature \( T_g \), and an increase in solvent content generally results in lower relaxation enthalpy, faster relaxation rates, prolonged ductility and a reduction of \( T_g \), which increases the alloys’ susceptibility to room-temperature crystallization. The results also show that chemical bonding and specific topologies contribute to relaxation kinetics, where alloys with greater mixing enthalpies and greater differences in atomic radii between the constituents exhibit greater relaxation enthalpies and relaxation rates. In conclusion, we present design concepts towards enhancing long-term ductility in Mg-based glasses via a delicate balancing of their chemistry and topology.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Due to their low density, high specific strength and high elastic limit, magnesium-based alloys are of emerging interest for use in aerospace, automotive and consumer electronics-based applications. Bulk amorphous alloys or bulk metallic glasses are a relatively new class of advanced metallic alloys which exhibit extraordinary properties for structural, mechanical and functional applications. They exhibit high strength (three times that of crystalline alloys) which approach the theoretical maximum strength [1], the highest elastic limits of all metallic materials (at least twice that of regular metals), and improved corrosion resistance. Amorphous alloys based on platinum and palladium, in particular, appear to possess the highest damage-tolerance of any material known to date [2,3].

Since the discovery of the \( \text{Mg}_{70}\text{Zn}_{30} \) metallic glass in 1977 [4], numerous Mg-based amorphous alloys or bulk metallic glasses have been developed. So far the majority of these glass-forming compositions have been based on Mg–TM–RE or Mg–TM–Ca ternary systems (where TM = transition metals Cu, Ni, Zn, Ag and RE = rare-earth metals Y, Gd, La, Nd, Ce, etc.) [5–11]. Some of these alloys have exceptional glass-forming ability with critical casting sizes of up to 27 mm [11]. Essentially, the key issue precluding the use of Mg-based glasses for at least small-scale structural applications is their inherent low fracture toughness or brittle nature. This shortfalls in mechanical performance is due to (i) the low activation energy of shear banding (which is directly associated with the chemistry of these glasses), and (ii) the rapid structural relaxation effects they exhibit [12–15]. Due to these glasses’ low glass transition temperatures (\( T_g \)) severe embrittlement can occur even at room temperature (corresponding to 0.7 \( T_g \)) and on relatively short timescales, strongly compromising their potential usefulness and commercial viability.

However, there are some examples which indicate a more positive design direction for these high-potential materials. In general, the ductility of Mg-based metallic glasses can be improved significantly by the incorporation of ductile crystalline phases [16,17]. Indeed, it has been found that the evolution of specific crystallites in an amorphous matrix can alleviate embrittlement induced by structural relaxation [18]. However, a significant volume fraction of crystallites in such a composite structure often often results in the deterioration of the superior strength and corrosion properties of metallic glass; further, composite microstructures are often difficult to produce, requiring specific cooling rates or specialized processing techniques [16–20]. Therefore this research focuses on design strategies for improving the ductility of fully amorphous specimens.
Considerable ductility in amorphous ribbons has been reported by Gu et al. in Mg–Zn–Ca alloys with Mg concentrations from 68 to 85 at% [5]; by Guo et al. in the Mg–Cu–Ca, Mg–Cu–Y and Mg–Ni–Y systems for alloys with a Mg content >85 at% [21]; and by Yu et al. in Mg–Zn–Ca–Yb alloys [22]. Modest ‘bulk’ glass ductility has also been observed in Mg-rich Mg–Ni–Gd-based [10,23] and Mg–Ni–Ca [24] alloy systems, pointing to higher Mg-content as a first step in improving ductility. However, few reports offer the details of ductile performance over a prolonged period of time. Given that some of these ‘ductile’ alloys can completely embrittle at room temperature after 3–4 days [14,25,26], these details and a design approach for alleviating metallic glass embrittlement in long-term applications are critical if these materials are to be brought to the forefront of applied technology [9].

In this study we present experimental results for a broad range of Mg-based amorphous alloy compositions, focusing specifically on bending ductility or flexural performance over time at room temperature. The mechanical performance of these alloys is incrementally correlated with their thermal properties and changes in structural characteristics at regular time intervals. Based on these results, we devise a strategic direction for the future development of Mg-based glasses with extended toughness and service life.

2. Experimental procedure

Mg-based alloys were produced using high-purity elements Mg (99.99%, Cerac), Zn (99.99%, Alfa Aesar), Al (99.999%, Cerac), Cu (99.995%, Praxair), Ni (99.95%, Alfa Aesar), Ca (99.5%, Alfa Aesar), and Y (99.99%, Treibacher Industry). Alloys were prepared by induction melting in graphite crucibles. In the case of Mg–Cu–Y and Mg–Ni–Y elemental Mg was alloyed with eutectic Cu5Y10 and Ni5Y10 pre-alloys, which were prepared by arc-melting under high-purity (6N) Ar atmosphere. Amorphous Mg-based ribbons with thicknesses of 40–45 µm were produced using the melt spinning technique (Melt spinner HV, Edmund Buehler). Differential scanning calorimetry (DSC) measurements were performed on samples to determine thermal material parameters such as glass transition temperature \( T_g \), primary crystallization temperature \( T_c \), and the enthalpy related to structural relaxation. Measurements were carried out in graphite pans using a Seiko DSC 220 CU instrument at a heating rate of 20 Kmin\(^{-1}\) under a flow of high-purity argon. X-ray diffraction (XRD) data were acquired using a STOE diffractometer (STADI P) and a monochromatic CoK\(_\alpha\) radiation source for Mg–Zn-based alloys and a CuK\(_\alpha\) source for Mg–[Cu,Ni]-based alloys. The measurements were performed in Bragg-Brentano geometry with a fixed incoming angle of 20° and using a 140° image plate detector (STOE, IP-PSD). Vickers hardness values were obtained using a micro-hardness testing device (MXT-x, Wolpert).

Bending tests were performed using a digital micrometer setup at room temperature similar to that used in Refs. [13,14,26]. The ribbon samples were clamped between two micrometer platen faces as shown in Fig. 1. The micrometer screw was turned incrementally to smaller distances, resulting in a gradual increase in ribbon bending strain. Three modes of ribbon response were considered: ductile, buckling and brittle fracture. Here we define brittle as a ribbon that fractured completely during bend testing. Buckling ribbons did not completely fracture, but had clearly failed and could not sustain further plastic deformation, and ductile ribbons exhibited no fracture or buckling behavior and remained completely intact and plastic.

The fracture or buckling distances, \( d \), were determined for each alloy at specific times after manufacturing. The bending strain, \( \varepsilon_{f/b} \), for fracture or buckling was evaluated by

\[
\varepsilon_{f/b} = t / (d - t),
\]

where \( t \) is the thickness of the ribbon. Here, \( \varepsilon_{f/b} = 1 \) or 100% when \( d = 2t \), i.e. when the ribbon has bent completely and doubled its thickness. Each test was repeated 5 times per alloy at specific time increments after manufacture.

Ribbons were held at room temperature for the duration of the study and characterized structurally (using XRD), thermophysically (using DSC) and mechanically (using the bend testing method) at specific time intervals after manufacture. Typical testing time increments were <1 day, 1 week, 1 month and 3 months, but time intervals were adjusted for more relaxation-prone compositions. It was noted that there was some fluctuation in strain-to-failure data in the buckling regime because of difficulties in determining the precise buckling point, given that these samples did not completely fracture.

3. Results

Table 1 gives the nominal alloy compositions, characteristic thermo-physical properties, relaxation-related parameters, time to embrittlement, and Vickers hardness of the alloys examined in this study. The time to embrittlement is defined as the time at which the ribbon bending response departs from fully ductile behavior within the bounds of the testing schedule. Due to the release of enthalpy associated with structural relaxation, the glass transition temperatures reported here are determined in the later stages of aging.

3.1. Time-dependent bending ductility and hardness

Fig. 2 shows the bending performance of the compositions studied as a function of room-temperature aging, where respective bending strains have been calculated using Equation (1). It illustrates the influence of different alloy constituents (chemistry) and various topologies.

Fig. 2(a) focuses on binary Mg–Zn metallic glasses showing abrupt embrittlement to the buckling regime for Mg70Zn30 after 2 days, whereas Mg75Zn25 remains ductile for 20 days before becoming brittle. Fig. 2(b) shows results for Mg–Zn–Ca alloys for a fixed Ca concentration of 5 at%. Here the alloy with the highest Mg-content, Mg53Zn17Ca5, remains ductile for the full duration of testing, whereas those with reduced Mg-content, Mg70Zn25Ca5 and Mg67Zn28Ca5, embrittle after 14 and 2 days, respectively. Fig. 2(C) gives data for the Mg–Zn–Al system with a fixed Al-content of...
5 at.% and the Mg–Zn–La system with a fixed La-content of 3 at.%. Interestingly, the Mg–Zn–Al alloys do not completely embrittle over the testing duration, with the higher Mg-content alloy Mg74Zn21Al5 remaining completely ductile and the Mg70Zn25Al5 maintaining some structural integrity in the ductile and buckling regime thereafter. Mg–Zn–La alloys appear ductile at considerably higher Mg-content (e.g. Mg77Zn20La3), whereas the Mg72Zn25La3 alloy exhibits no ductile behavior after 1 day of production. Fig. 2(d) shows bending data for Mg85Cu5Y10 and Mg85Ni5Y10 alloys with considerably higher Mg-content. Here, the Cu-containing alloy embrittles within 2 days of production and the bending strain which the sample can accommodate continues to degrade over the period of a week (see also Ref. [14]). This is a notable improvement on data reported for the Mg-lean Mg65Cu25Y10 composition, which embrittles completely within 2 h of casting [14]. In contrast to the Mg–Cu–Y system, the Mg85Ni5Y10 alloy remains completely ductile for the test duration, whereas the Mg-lean Mg60Ni30Y10 alloy is brittle immediately after production [27]. It can be seen here that amorphous alloys with higher Mg-content generally exhibit improved ductility within a given alloy system. In particular cases, some alloys remain fully ductile after three months of room-temperature aging, namely the

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_{onset} ) [K]</th>
<th>( T_g ) [K]</th>
<th>( T_x ) [K]</th>
<th>( \Delta H_{eq} ) [J/g]</th>
<th>( \tau ) [days]</th>
<th>( \beta )</th>
<th>( t_B ) [days]</th>
<th>Hardness [HV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg75Zn25</td>
<td>333</td>
<td>344</td>
<td>359</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>20</td>
<td>191 ± 2.5</td>
</tr>
<tr>
<td>Mg70Zn30</td>
<td>335</td>
<td>352</td>
<td>374</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2</td>
<td>220 ± 5.4</td>
</tr>
<tr>
<td>Mg74Zn21Ca5</td>
<td>336</td>
<td>351</td>
<td>369</td>
<td>7.64</td>
<td>14.106</td>
<td>0.479</td>
<td>&gt;90</td>
<td>206 ± 6.1</td>
</tr>
<tr>
<td>Mg70Zn25Ca5</td>
<td>340</td>
<td>353</td>
<td>370</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>14</td>
<td>210 ± 3.9</td>
</tr>
<tr>
<td>Mg67Zn28Cu5</td>
<td>338</td>
<td>359</td>
<td>374</td>
<td>10.07</td>
<td>8.07</td>
<td>0.466</td>
<td>2</td>
<td>223 ± 1.2</td>
</tr>
<tr>
<td>Mg74Zn21Al5</td>
<td>337</td>
<td>348</td>
<td>365</td>
<td>5.52</td>
<td>14.43</td>
<td>0.405</td>
<td>&gt;90</td>
<td>191 ± 3.2</td>
</tr>
<tr>
<td>Mg70Zn25Al5</td>
<td>338</td>
<td>350</td>
<td>377</td>
<td>5.90</td>
<td>14.96</td>
<td>0.375</td>
<td>4</td>
<td>209 ± 6.2</td>
</tr>
<tr>
<td>Mg72Zn25La3</td>
<td>335</td>
<td>338</td>
<td>366</td>
<td>3.24</td>
<td>11.26</td>
<td>0.434</td>
<td>&gt;90</td>
<td>206 ± 4.5</td>
</tr>
<tr>
<td>Mg74Zn21Al5</td>
<td>337</td>
<td>342</td>
<td>374</td>
<td>3.94</td>
<td>5.93</td>
<td>0.286</td>
<td>&lt;1</td>
<td>218 ± 1.5</td>
</tr>
<tr>
<td>Mg67Zn28Cu5</td>
<td>359</td>
<td>430</td>
<td>450</td>
<td>10.65</td>
<td>4.56</td>
<td>1.260</td>
<td>1</td>
<td>205 ± 27</td>
</tr>
<tr>
<td>Mg85Ni5Y10</td>
<td>378</td>
<td>450</td>
<td>467</td>
<td>10.99</td>
<td>12.08</td>
<td>0.960</td>
<td>&gt;90</td>
<td>210 ± 27</td>
</tr>
<tr>
<td>Mg60Ni30Y10</td>
<td>–</td>
<td>482</td>
<td>467</td>
<td>12.08</td>
<td>0.960</td>
<td>&gt;90</td>
<td>–</td>
<td>210 ± 27</td>
</tr>
</tbody>
</table>

\( a \) \( T_g \) and \( T_x \) data are taken at the stage of relaxation of 90 days for all alloys, with the exception of Mg75Zn25, for which the thermal properties were evaluated after 30 days.

\( b \) This sample was measured at 30 days, at which point it had substantially crystallized.

\( c \) This sample showed minor evidence of crystallites in the as-cast state.

Fig. 2. Bending strain of Mg-based amorphous ribbons over time and specific failure mode in (a) Mg–Zn binary alloys; (b) Mg–Zn–Ca alloys; (c) Mg–Zn–Al and Mg–Zn–La alloys; and (d) Mg–Ni–Y and Mg–Cu–Y alloys.
Mg$_{74}$Zn$_{21}$Ca$_5$, Mg$_{72}$Zn$_{21}$Al$_2$, Mg$_{72}$Zn$_{20}$La$_3$ and Mg$_{85}$Ni$_5$Y$_{10}$ metallic glasses. It is also interesting to note that the Mg$_{74}$Zn$_{21}$Al$_5$ and Mg$_{85}$Ni$_5$Y$_{10}$ amorphous alloys display prolonged ductility well beyond the timeframe of this study. It is also evident from Table 1 that in the as-cast state, the hardness of these metallic glasses tends to decrease with increasing Mg-content, and hardness generally increases over time, which is likely the result of structural relaxation/densiﬁcation [25,28].

3.2. Calorimetric investigation and XRD analysis

In order to capture important relaxation and crystallization events that identify ductile-to-brittle transitions over time, complementary DSC and XRD data were also gathered. Both the exothermic relaxation below $T_g$ and the enthalpic height of the glass transition peak are related to the excess structural free volume of the material. Changes in enthalpy can be linearly correlated with free volume changes associated with structural relaxation [25,29–35]. Figs. 3–7 show time-incremented DSC and XRD traces for the Mg-based amorphous alloys investigated.

Fig. 3(a) shows data for the Mg$_{75}$Zn$_{25}$ metallic glass. Here the DSC trace taken at <1 day shows a distinct structural relaxation enthalpy release, between 333 K and 370 K, which quickly diminishes over 30 days of room-temperature aging, revealing $T_g$. Within this time frame the alloy undergoes embrittlement, and after 60 days the glass transition and the first crystallization peak disappear, indicating the completion of the primary crystallization reactions. The secondary crystallization reactions at temperatures above 500 K have also been altered substantially due to the room-temperature crystallization events of the primary phases at 60 and 90 days. Fig. 3(b) shows that the Mg$_{75}$Zn$_{25}$ alloy has started crystallizing after 7 days of aging and the alloy continues to crystallize into a range of equilibrium and metastable phases, namely Mg, Mg$_{51}$Zn$_{20}$ and MgZn [36]. It seems that initially this small volume fraction of crystallites does not affect bending performance, and nor does it signiﬁcantly affect the DSC response up to 30 days.

Fig. 3(c) shows DSC data for the Mg$_{70}$Zn$_{30}$ metallic glass. Here a subtle enthalpy release beginning at around 335 K is evident. Following this, distinct differences in the enthalpy release prior to $T_g$ between 1 and 90 days are prominent, decreasing in intensity over time. This enthalpy release is not present after 90 days, where the inflection related to $T_g$ is now observable. However, these data show no distinct correlation with the mechanical embrittlement observed in Fig. 2(a). Fig. 3(d) indicates that the Mg$_{70}$Zn$_{30}$ alloy remains amorphous within the resolution of XRD for 90 days.

Fig. 4 shows DSC and XRD data for three Mg–Zn–Ca alloys. The <1 day traces highlight a large enthalpy release associated with a relatively high degree of structural relaxation. Here a speciﬁc trend in structural relaxation and chemistry emerges, where alloys with a higher Mg-content have lower $T_g$ and $T_x$ onset temperatures.

Fig. 3. (a) and (c) DSC traces of the Mg$_{75}$Zn$_{25}$ and Mg$_{70}$Zn$_{30}$ amorphous ribbons, and (b) and (d) corresponding XRD data taken at speciﬁc time increments. Insets in (a) and (c): Magniﬁcation of the region prior to the glass transition and crystallization events associated with structural relaxation.
Similarly the onset temperature of relaxation prior to \( T_g \) in the as-cast state also tends to shift to lower temperatures with increasing Mg-content. All Mg–Zn–Ca metallic glasses remained amorphous throughout the duration of this study.

Fig. 5(a)–(d) shows DSC and XRD results for Mg74Zn21Al5 and Mg70Zn25Al5 amorphous alloys. These alloys exhibit a considerable relaxation enthalpy release prior to \( T_g \) within 7 days of aging. This correlates well with the mechanical data for Mg70Zn25Al5, which embrittles substantially after 4 days. However, this is not the case for Mg74Zn21Al5, which maintains complete ductility over 90 days and beyond. The total enthalpy release associated with relaxation of these alloys over 90 days is considerably less than that of the Mg–Zn–Ca alloys, yet slightly greater than that of the binary Mg–Zn alloys with similar Mg-content. Despite the clear shift in composition and \( T_g \), the onset of the relaxation event in the as-cast state begins at 337 K and 338 K for Mg74Zn21Al5 and Mg70Zn25Al5, respectively, which correlates well with their similar \( T_g \) values of 348 K and 350 K. Fig. 5(b) reveals that the Mg74Zn21Al5 amorphous alloy devitrified partially between 30 and 90 days of aging, where a shoulder is evident on the amorphous halo at 40–41° 20 after 30 days which develops into crystal peaks after 90 days. The majority of these peaks can be indexed as \( \alpha\)-Mg. There is also evidence of trace amounts of the metastable Mg51Zn20 crystalline phase in the later stages of aging, which correlates well with similar devitrification studies of this system [37]. This suggests that the presence of \( \alpha\)-Mg in this alloy may promote ductility.

Fig. 6 shows DSC and XRD results for the Mg77Zn20La3 and Mg72Zn25La3 amorphous alloys. These show a very low enthalpy release associated with relaxation over 90 days, similar to the binary Mg–Zn glasses. This is likely a result of the relatively high Mg-content and low (only 3 at.%) solute addition of La. This slow enthalpy release/relaxation corresponds well to the mechanical testing results, where the Mg77Zn20La3 alloy remains ductile for the entire 90 days and the Mg72Zn25La3 alloy’s ability to accommodate strain diminishes very slowly over time. The \( T_g \) of these alloys is not so evident. For the Mg77Zn20La3 alloy a shallow, reproducible exothermic reaction attributed to the precipitation of \( \alpha\)-Mg (similar to that observed in Mg75Zn25) is evident. Fig. 6(b) indicates the presence of \( \alpha\)-Mg in the as-cast microstructure of the ribbon, which was also reported in Ref. [18] for this alloy. This figure also indicates that the ribbon contains a trace amount of the metastable Mg51Zn20 phase after 90 days of aging, similar to the Mg74Zn21Al5 alloy, which may assist in maintaining this alloy’s bending ductility. Given the relatively weak \( T_g \) signal and low relaxation enthalpy for these Mg–Zn–La alloys and the presence of crystallites in Mg77Zn20La3, it can be assumed that their glass-forming ability is fairly low.
Fig. 7 shows data for the high Mg-content Mg$_{85}$Cu$_{5}$Y$_{10}$ and Mg$_{85}$Ni$_{5}$Y$_{10}$ amorphous alloys measured in the as-cast state, and after several days and >2 years of room-temperature relaxation. In both alloys most relaxation occurs rapidly within several days of production, in agreement with previous studies [14,25,26]. Despite their relatively high Mg-content, it is expected that the thermal stability of these alloys over time is quite high given their relatively high $T_g$. This is probably a result of the high Y content. DSC traces shown in Fig. 7(b) for the Mg$_{85}$Ni$_{5}$Y$_{10}$ alloy show that the relaxation event is almost completely detached from $T_g$, occurring and completing at a substantially lower temperature. Furthermore, XRD traces of the Mg$_{85}$Cu$_{5}$Y$_{10}$ and Mg$_{85}$Ni$_{5}$Y$_{10}$ alloys show that these alloys do not crystallize within 2 years of room-temperature aging.

In most cases considerable enthalpy release associated with structural relaxation prior to $T_g$ and $T_x$ has been observed here, particularly in alloys relaxed for less than one day (generally within 1 h of casting). Differences in enthalpy release over time can be linearly correlated with free volume changes associated with structural relaxation [25,29–35],

$$\Delta H = \alpha \Delta \nu,$$  \hspace{1cm} (2)

where $\Delta H$ is the difference in enthalpy released between the as-cast (unrelaxed) and relaxed states, $\alpha$ is a relaxation rate constant, and $\Delta \nu$ is the free volume concentration change due to relaxation. It has been shown that the kinetics of free-volume related relaxation in the sub-$T_g$ region can be accurately described by a stretched exponential relaxation function [31–35], known as the Kohlrausch-Williams-Watts equation,

$$\varphi(t) = \exp \left[ - \left( \frac{t}{\tau} \right)^\beta \right],$$  \hspace{1cm} (3)

where $t_a$ is the annealing time, $\tau$ is the average enthalpy relaxation time, and $\beta$ is the Kohlrausch exponent. Hence, the enthalpy of relaxation for a given time increment and relaxation temperature, $\Delta H(t_a)$, is given by Refs. [31–35]:

$$\Delta H(t_a) = \Delta H_{eq} \left[ 1 - \exp \left[ - \left( \frac{t_a}{\tau} \right)^\beta \right] \right],$$  \hspace{1cm} (4)

where $\Delta H_{eq}$ is the equilibrium value of $\Delta H$ as $t_a$ approaches infinity for a given temperature. Fig. 8 plots the relaxation enthalpy changes obtained from DSC with respect to the as-cast condition over the available time periods for all compositions investigated. A stretched exponential curve was fitted to each data set containing four or more data points in accordance with Equation (4), allowing the determination of characteristic relaxation-related parameters, such as the equilibrium relaxation enthalpy $\Delta H_{eq}$, the average enthalpy relaxation time $\tau$, and the Kohlrausch exponent $\beta$. These parameters allow for a direct quantitative comparison of relaxation phenomena among these alloys. The corresponding values are reported in Table 1.
It is found that for a given alloy system the equilibrium enthalpy release, $\Delta H_{eq}$, tends to increase with decreasing Mg-content, which probably results from the rearrangement of atomic bonds between dissimilar atoms (which have a higher bond enthalpy than similar atom bonds) during relaxation in higher solute-content alloys. The average enthalpy relaxation time, $t$, and Kohlrausch exponent, $b$, increase with increasing Mg-content for a given alloy system. Despite having considerably higher $T_g$ and $T_x$ values, the Mg$_{85}$Cu$_5$Y$_{10}$ and Mg$_{85}$Ni$_5$Y$_{10}$ alloys relax considerably faster than the Mg–Zn-based alloy systems. These trends are related to the ease of structural rearrangement due to chemical and topological effects. The relative amount of heat (enthalpy) released upon relaxation also correlates with the heat of mixing between constituents and the relative amount of these constituents present, particularly for the third atom additions to the Mg–Zn-based alloys.

4. Discussion

The proliferation and dynamics of shear bands and hence the ability of a metallic glass to accommodate strain are essentially a result of the inherent physical and chemical properties of the glass [28,38,39]. In the following we discuss the critical factors affecting the mechanical response of the Mg-based glasses studied. We focus on the effects of chemistry, topology, structural relaxation and thermal stability. Finally, we present a design concept for enhancing long-term ductility.

4.1. Effects of chemistry on mechanical response

Bonding in metallic glasses is essentially metallic in nature. During deformation, bonds are broken and re-formed, and the ease with which this occurs depends on the specific bond strength, rigidity or preferred angularity of these bonds [28,40]. A material's response to deformation can be approached by considering its bulk ($K$) and shear ($G$) moduli, which account for atomic bond stretching or compressing and bond distortion, respectively, and are strongly dependent on the underlying bonding state of the constituents [40]. A correlation between fracture energy and these elastic properties exists, where amorphous alloys with $G/K < 0.41$ or Poisson's ratio $\nu > 0.34$ are tough and exhibit large plastic strain to failure, while those with $G/K > 0.43$ or $\nu < 0.32$ are brittle [2,3,26,40–43].

A molecular dynamics study of Mg–Zn and Mg–Zn–Ca metallic glasses by Mahjoub et al. [44] showed how elastic constants are dramatically affected by composition. An increase in Mg-content decreased the alloys' shear modulus (and thus increased the Poisson's ratio), and the shear modulus was also found to be highly sensitive to the Ca content. This was correlated with the electronic density of states of the species within the amorphous structure, where minimizing solute elements that exhibit large electronic charge transfer with the solvent species reduced the alloys' shear modulus (and thus increased the Poisson's ratio). This effect was demonstrated through simulations and experimentally for other alloy systems and has been qualitatively linked to mixing enthalpy.

![Fig. 6](image-url)
and electronegativity among the constituents [7,10,21,24,45–49]. This phenomenon is reflected in the findings of this study, where alloys with higher Mg-content and low amounts of high charge-transferring elements such as Ca, La and Y (which have high mixing enthalpies with Mg [50] compared to e.g. Zn or Al) exhibit higher ductility in the as-cast and progressively aging states.

Despite having the same Mg-concentration, Mg85Cu5Y10 and Mg85Ni5Y10 amorphous alloys show completely differing mechanical behavior. Ni has a slightly higher mixing enthalpy with Mg compared to Cu [48], but, as with other group 10 elements (including Pd and Pt), it can exhibit a reduced oxidation/valence state of zero (i.e. a filled d-shell of electrons). In terms of chemical bonding, these elements have the potential to provide the ‘most metallic-type’ bonds in terms of charge transfer and bond-angle freedom, which potentially explains why Pd- and Pt-based glasses exhibit very high Poisson’s ratios and the highest toughness of all glassy materials. It is also apparent from this work, and other reports [5,6,18,21], that adding divalent Ca at the expense of trivalent rare-earth elements (such as Y or La) promotes improvements in ductility. Our results also show that completely amorphous alloys become harder (stronger) with increasing solute content, in particular in alloys containing Y and La (see Table 1).

### 4.2. Effects of structure/topology on mechanical response

The local distribution and ease of re-distribution of free volume governs metallic glass deformation characteristics. The macroscopic plastic deformation of a metallic glass (perceived as ductility) is essentially the sum of local strains accommodated via...
the operation of multiple shear transformation zones (STZs) and the redistribution of free volume [28,51,52]. Here a structure consisting of higher free volume will more readily accommodate local shear events, and free volume is inherent in glass processing (cooling rate/degree of relaxation) and its composition-specific topology. Atomistic simulations have shown that short-range topological and chemical ordering affects shear [53,54]. Shear-band initiation and propagation are also found to differ due to differences in local atomic structure and chemistry [55–57]. Glasses that contain more ‘liquid-like’ atomic structures (highly distorted polyhedra or high-free-volume configurations) are known to feature improved ductility and typically have high solvent content [2,48,57–61].

Within the results presented, despite their distinct differences in chemistry there are also distinct structural/topological differences in the systems investigated due to the varying atomic radii of their constituents (Mg = 160 pm, Cu = 127 pm, Ni = 126 pm, Zn = 139 pm, Al = 141 pm, La = 187 pm, Ca = 197 pm [62]). Outlined by the results of this and other work [6–8,10,13–15,27], Cu- and Ni-containing Mg-alloys (where Cu and Ni have lower coordination numbers than Zn or Al) require a considerably greater Mg-content to exhibit ductility. There may also be a similar topological effect when small amounts of larger elements are added, where Ca atoms promote ductility at lower Mg-concentrations compared to slightly smaller rare-earth elements [18,21].

4.3. Effects of structural relaxation on mechanical response

The major drawback of structural relaxation in metallic glasses is the progressive annihilation of structural free volume. The amount and distribution of free volume governs metallic glass plasticity, and hence structural relaxation has a pronounced effect on mechanical response. Structural relaxation is known to promote an increase in $K$ due to a reduction in interatomic spacing [28,41,63]. However, this also leads to an even greater increase in $G$ hindering STZ operation and thus generating an overall reduction in toughness [26,28,41,63–67]. A reduction in free volume may also suppress shear-banding susceptibility (the number density of shear events) and the radius ratios of the amorphous alloy gradually advances towards a state less favorable for metallic glass ductility and toughness. The initial properties of the alloy (which are chemistry- and structure-dependent) and the rate at which relaxation occurs dictate the time needed for an alloy to cross the ductile-to-brittle transition. Hence if an alloy does not cross this transition after complete structural relaxation it will theoretically remain ductile.

In extreme cases, where the aging temperature is high enough for atomic diffusivity, i.e. relatively close to $T_g$ and $T_x$, the ongoing relaxation of the metastable amorphous structure can lead to crystallization below $T_g$ [37,68]. The density of an ordered crystal structure will differ from that of the vitreous solid, and thus when a crystal precipitates within the glass there is a local volumetric change inducing a localized stress within the amorphous matrix which can generate mechanical instability. The type of precipitating crystal can also affect the mechanical response of a partially devitrified glass, whereby a ductile solid-solution phase (e.g. $\alpha$-Mg) is much preferred over a brittle intermetallic phase because of its ability to accommodate strain and effectively ‘absorb’ shear bands. This is illustrated in this study by the progressive bending response of the Mg$_{72}$Zn$_{28}$ alloy, which crystallizes significantly during aging. In this case the precipitation of primarily Mg$_5$Zn$_2$ quickly degrades bending ductility, whereas for Mg$_{74}$Zn$_{13}$Al$_5$ and Mg$_{77}$Zn$_{20}$La$_3$ the presence of $\alpha$-Mg supports ductility in a way similar to other Mg-based composites [16–18].

4.4. Effects of thermal stability on structural relaxation rates and shear-band dynamics

Higher $T_a$ and $T_x$ appear to slow relaxation processes and lower an alloy’s susceptibility to ambient temperature crystallization. Results show that for a given alloy system, increasing Mg-content corresponds to a reduction in $T_a$; and for Mg$_{72}$Zn$_{25}$, Mg$_{70}$Zn$_{30}$, Mg$_{92}$Zn$_{18}$Al$_5$ and Mg$_{77}$Zn$_{20}$La$_3$ alloys, which exhibit low $T_a$ values, relative degrees of crystallization are observed. Similar trends have been reported for Mg–Zn [36] and Mg–Al–Ca alloys [69], where crystallite volume fraction after room-temperature aging increases with increasing Mg-content. Based on the results presented here and those found in literature, alloys with a $T_a < 350$ K and $T_x < 369$ K have a great tendency to crystallize at room temperature within less than 90 days.

The rate of structural relaxation is related to the diffusion and annihilition of structural free volume and can be clearly deduced from the data in Fig. 8 for the alloys studied here. The relaxation rate is mathematically represented by the Kohlrausch exponent, $\beta$, given in Table 1. It has been recognized that $\beta$ is the consequence of the degree of cooperativity in the rearrangement of structural units within a glass [34,70], and $\beta < 1$ reflects a broad distribution of relaxation times and structural rearrangements rather than a single (Debye-like) relaxation time/event. From a chemistry standpoint, alloys which contain large quantities of rare-earth elements, such as Mg$_{85}$Cu$_5$Y$_{10}$ and Mg$_{85}$Ni$_5$Y$_{10}$, and also exhibit high mixing enthalpies between the components, relax quite rapidly with a $\beta$ close to 1. Even for the Mg–Zn-based alloys, where $\beta$ is around 0.4, alloys which contain 5 at.% Ca and 3 at.% La tend to relax faster than the Mg–Zn or Mg–Zn–Al alloys with similar Mg-content. Here the evolution of specific chemical short-range order (between elements with more negative heat of mixing, for example) may contribute to rapid or more cooperative rearrangement sequences of atoms during relaxation.

From a structural/topological perspective, the Mg$_{85}$Cu$_5$Y$_{10}$ and Mg$_{85}$Ni$_5$Y$_{10}$ alloys share a similar topological structure (both possessing constituents of similar atomic radii), which differs greatly from that of the Mg–Zn-based glasses. Fig. 8 reveals a strong correlation between relaxation rate (or $\beta$) and the radius ratios of the smallest and largest alloy constituents, i.e. the smaller the radius ratio between the largest and smallest elements in the system, the faster the relaxation rate. Correspondingly, Mg$_{85}$Cu$_5$Ni$_5$Y$_{10}$ alloys relax fastest, followed by Mg–Zn–Ca, Mg–Zn–La, Mg–Zn–Al, and the Mg–Zn binary. Individual diffusion constants aside, this indicates that the specific topologies generated by such atomic size distributions may have an inherent geometry-based structural free volume which affects atomic mobility during relaxation.

From a mechanical standpoint, relationships between thermal stability (or $T_a$), the activation of shear, and shear-band dynamics are somewhat ambiguous. Shear-band initiation sites (zones of increased free volume) require a high $T_a$ to thermally stabilize them against annihilation at room temperature [71]. However, an increase in $T_a$ may be accompanied by an unfavorable change in elastic properties (such as that observed when increasing solute content in Mg–Zn–Ca alloys [44]), making successful shear activation less probable [72]. Stable shearing (slow shear-band dynamics) is promoted by strong bonds and small shear activation stresses [57]. Although an increase in $T_a$ cannot guarantee an increase in bond strength, it is likely to promote an increase in the critical stress for shear activation, which is unfavorable for stable
shear-band sliding as it lowers the activation barrier for shear-band dynamics [57,73,74]. This said, the most ductile Mg-based bulk metallic glasses are Mg–Ni–Gd-based (again, notably containing Ni) which exhibit significant plastic, serrated flow deformation characteristics and the highest reported $T_g$ values [6,10].

Although this study focuses primarily on samples in ribbon form, we recognize that there is a significant trade-off between glass-forming ability and ductility. It is well known that significant solute additions are essential to maintain the high chemical and topological entropy contributions associated with low critical cooling rates and high glass-forming ability, which is the antithesis of the requirements for ductility found in this work.

4.5. Design strategy for the development of ductile Mg-based metallic glasses

In order to maintain high ductility, even after complete structural relaxation, it becomes clear from this work and from the literature that a high Mg-content is essential. It is also clear that solute elements which have a higher tendency for transferring electrons or contribute strongly to bond hybridization should be minimized or avoided, whereas those with potentially full electron shells should be utilized where possible. These results also infer that alloy topologies which contain elements with larger solute radii similar to Zn or Al (–140 pm) as opposed to Cu or Ni (–126 pm) may have an inherent topological advantage, resulting in significantly slower relaxation rates and longer relaxation times. Given that $T_g$ and thermal stability tend to decrease with increasing Mg-content, alloying of elements with higher melting points is also preferred in the attempt to increase thermal stability and thus to reduce structural relaxation rates. Here these underlying characteristics have provided sustained ductility in Mg–Zn–Ca, Mg–Zn–Al, Mg–Zn–La, Mg–Ni–Y, Mg–Zn–Ca–Yb [21], and Mg–Cu–Ca [22] metallic glass ribbons; and in Mg–Ni–Ca [7] and Mg–Ni–Gd [6,10] bulk metallic glasses. However, compositionally a delicate balance between elastic properties, strength and hardness, thermal stability, and glass-forming ability needs to be considered.

Based on these critical aspects, high-potential alloying candidates for the development of next-generation Mg-based (bulk) metallic glasses with improved ductility, high thermal stability, and fracture toughness should include combinations of Pd, Pt, Ni, Ca, and/or Yb. A thorough investigation of the glass-forming range, and thermal and mechanical characterization of these novel alloys, is currently underway and will be reported elsewhere.

5. Conclusions

Although the room-temperature structural relaxation of Mg-based amorphous alloys may be inevitable, we have identified several alloy compositions that overcome the embrittling effects of structural relaxation over a prolonged period of time (90 days). These include Mg$_{72.12}$Zn$_{12.12}$Ca$_{7.12}$Al$_{3.12}$, Mg$_{72.12}$Zn$_{12.12}$Al$_{3.12}$ and Mg$_{68.12}$Ni$_{31.12}$Y$_{10}$. We have seen that several key factors contribute to the extended ductility lifetime of these and other alloys found in literature. In summary, the solution to the challenge of ductility versus embrittlement due to structural relaxation in Mg-based glasses appears to be a matter of chemistry and topology. Tailoring the elastic modulus of the alloy for improving ductility is achieved in two ways: first, through minimizing chemical bond potential (i.e. maximizing Mg-content and minimizing solute additions that exhibit a large bond potential/charge transfer with Mg); and second through maximizing structural free volume by selecting specific compositions and alloying elements that provide ‘liquid-like’ structures and inherently high free-volume topologies. To arrest or dramatically hinder the rate of structural relaxation and possible crystallization, thermal stability must be increased via alloy chemistry, e.g. via reducing the Mg-content and alloying with higher melting point solutes that have higher bond potentials. These aspects are, however, mutually exclusive and a delicate balance between these and other aspects such as glass-forming ability need to be maintained to find future applications for these exceptional materials.

Acknowledgments

The authors thank Bruno Zberg (now at Straumann AG) and Daniel Ehler for providing various DSC data taken during their tenure at ETH Zurich.

References

[19] X. Zhou, K.D. Ralston, K.J. Laws, J.D. Cao, K.G. Gupta, M. Ferry, N. Birbilis, Effect of the degree of crystallinity on the electrochemical behaviour of Mg$_6$Cu$_{25}$Y$_{10}$ and Mg$_{68}$Zn$_{25}$Ca$_{10}$ bulk metallic glasses, Corrosion 69 (2013) 781–792.
G. Ravichandran, A. Molinari, Analysis of shear banding in metallic glasses
R. Mahjoub, K.J. Laws, J.P. Scicluna, J.E. Daniels, M. Ferry, A
X.J. Gu, A.G. McDermott, S.J. Poon, G.J. Shi
J.J. Lewandowski, W.H. Wang, A.L. Greer, Intrinsic plasticity or brittleness of
H. Horikiri, A. Kato, A. Inoue, T. Masumoto, New Mg-based metallic alloys
A. Castellero, D.I. Uhlenhaut, B. Moser, J.F. L
X.J. Gu, S.J. Poon, G.J. Shi
V. Wessels, G. Le Men
A. Takeuchi, A. Inoue, Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the major alloying element, Mater. Trans. 46 (2005) 2817–2829.