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Letter

Synthesis of Ag-based bulk metallic glass in the Ag–Mg–Ca–[Cu] alloy system

Kevin J. Laws[a,b,*], Karl F. Shamlaye[a,b], Michael Ferry[a,b]

[a] Australian Research Council Centre of Excellence for Design in Light Metals, Australia
[b] School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

A number of novel silver-based bulk metallic glasses from the Ag–Mg–Ca ternary and Ag–Mg–Ca–Cu quaternary alloy systems have been discovered. These amorphous alloys are located over a broad composition range from (at.%): 30 to 61% Ag, 7 to 38% Mg, 7 to 30% Ca and 0 to 15% Cu often far from ternary eutectic reactions. These new amorphous alloys have been developed in light of their potential applications as functional materials with high electrical and thermal conductivity combined with the superplastic formability of a metallic glass. Reported are the critical casting size and thermophysical properties of these bulk glassy alloys.

1. Introduction

The considerable research interest in amorphous alloys over recent years has led to the discovery of numerous multi-component bulk metallic glass (BMG) compositions in a broad range of base metals. Of the metallic elements, silver has been of high significance to commercial enterprise in the form of currency, commodity and jewellery. Since elemental silver has the highest thermal- and electrical-conductivity and light reflectivity of all metals, it has been used extensively in the electronics industry, optics, jewellery and as mirror-glass backings. The discovery of an amorphous Ag-based material with properties unique to both silver and the glassy state may prove highly significant in a range of new technological applications.

The crystallization of an alloy melt is a diffusion-based process, driven by thermodynamics and kinetics. In a thermodynamic sense, particular elements may be alloyed in specific concentrations such that the crystallization of high melting point intermetallics is avoided and mixing is promoted. On the other hand, the ability to slow crystallization kinetics when cooling from the molten state may be achieved topologically by selecting elements of a large atomic radius [1,2] and selecting elements of specific radius ratios in order to provide dense atomic packing configurations [3].

The Ag–Mg–Ca ternary and Ag–Mg–Ca–Cu quaternary systems were selected for detailed analysis, since: (i) all elements have simple electronic structures and are thermodynamically compatible, forming multiple deep binary eutectics and relatively low temperature intermetallics with relatively similar negative (with the exception of Ag–Cu) heats of mixing (dependent on composition); (ii) each of the constituent elements display a large difference in atomic radius and the required specific radius ratios favoured for glass formation (Cu – 128 pm, Ag – 144 pm, Mg – 160 pm, and Ca – 196 pm), which geometrically allows for a larger compositional range of efficiently packed clusters [3,4], and (iii) glass formation in the binary Ag–Ca system has been reported over a broad composition range [5] and high GFA in the Ca-rich region of both the Ag–Mg–Ca ternary and Ag–Mg–Ca–Cu quaternary system has been confirmed by Amiya and Inoue [6], with the $Ca_{60}Mg_{20}Ag_{20}$ and $Ca_{60}Mg_{20}Ag_{10}Cu_{10}$ alloys exhibiting a critical casting diameter (D_C) of 4 and 7 mm, respectively. Copper was specifically selected for this work as it too has exceptionally high electrical and thermal conductivity and has a similar, simple electronic configuration to Ag with a full *d*-electron shell and single *s*-electron in its outer shell. Although the Ag–Cu couple is quoted as having a slightly positive heat of mixing, based on general charge transfer, it is unlikely that a direct repulsion or immiscibility will occur when Ag and Cu are in the presence of high Mg and Ca solute concentrations (amorphous Ag-based alloys have been successfully produced in Ag–Cu–[Mg, Si, Sn, Sb] ternary systems using the melt spinning technique [7] and, also, binary Ag–Cu [8] and Ag–Cu–[Al, Ge, Mg] ternary amorphous films have been produced with crystallization temperatures ranging from 90 to 140 °C [9]).

2. Experimental procedures

Nominal alloy compositions determined to correspond to efficiently packed structures (shown in Table 1) were prepared using high purity metals – Ag (99.95 wt.%), Mg (99.85 wt.%), Ca (99.8 wt.%), Cu (99.9 wt.%) and a Mg/Ca master

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[*] Corresponding author at: School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia. Tel.: +61 422759375.
E-mail address: k.laws@unsw.edu.au (K.J. Laws).

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Table 1
Critical casting thickness (Z_C) and diameter (D_C), and thermophysical properties of Ag-based metallic glasses in the Ag–Mg–Ca ternary and Ag–Mg–Ca–Cu quaternary alloy systems.

Composition	Z_C	D_C	T_g [a]	T_X	T_m	T_l
$Ag_{61.5}Mg_{15.4}Ca_{23.1}$	0.7	1.0	213	253	392	647
$Ag_{61.5}Mg_{23.1}Ca_{15.4}$	0.5	–	167	212	513	646
$Ag_{53.8}Mg_{15.4}Ca_{30.8}$	0.8	1.0	171	225	380	539
$Ag_{53.8}Mg_{23.1}Ca_{23.1}$	0.7	1.0	178	215	384	614
$Ag_{46.2}Mg_{15.3}Ca_{38.4}$	0.3	–	134	166	381	536
$Ag_{46.2}Mg_{23.1}Ca_{30.7}$	0.7	1.0	126	153	406	492
$Ag_{46.2}Mg_{30.7}Ca_{23.1}$	0.5	–	120	154	405	607
$Ag_{38.4}Mg_{30.8}Ca_{30.8}$	0.5	–	121	153	475	532
$Ag_{38.4}Mg_{38.4}Ca_{23.2}$	1.1	1.5	118	152	488	523
$Ag_{53.8}Mg_{7.7}Ca_{30.5}Cu_{7.7}$	0.3	–	155	215	400	570
$Ag_{53.8}Mg_{15.4}Ca_{23.1}Cu_{7.7}$	0.5	–	160	190	394	558
$Ag_{53.8}Mg_{23.1}Ca_{15.4}Cu_{7.7}$	0.5	–	134	190	475	604
$Ag_{50}Mg_{11.5}Ca_{30.8}Cu_{7.7}$	1.0	1.5	179	214	396	536
$Ag_{50}Mg_{19.2}Ca_{23.1}Cu_{7.7}$	1.2	1.5	153	193	394	524
$Ag_{46.2}Mg_{15.4}Ca_{30.5}Cu_{7.7}$	0.8	1.0	141	172	360	532
$Ag_{46.2}Mg_{23.2}Ca_{23}Cu_{7.7}$	2.0	3.0	125	157	348	552
$Ag_{38.5}Mg_{23}Ca_{30.8}Cu_{7.7}$	2.0	3.0	111	143	424	581
$Ag_{38.5}Mg_{30.8}Ca_{23.1}Cu_{7.7}$	3.0	4.0	114	147	426	560
$Ag_{38.5}Mg_{38.5}Ca_{15.4}Cu_{7.7}$	0.5	–	132	163	438	569
$Ag_{30.8}Mg_{30.8}Ca_{30.8}Cu_{7.7}$	2.0	3.0	134	154	465	536
$Ag_{30.8}Mg_{23.1}Ca_{30.8}Cu_{15.4}$	2.5	3.0	140	159	461	530

[a] T_g values quoted here are the onset temperature of the glass transition.

alloy (99.8 wt.%). Alloys were prepared in BN-coated graphite crucibles by induction melting in a circulating argon (99.98 wt.%) atmosphere. Samples were produced by casting the alloys into a naturally cooled copper mould in a wedge configuration and various diameters using an inverted injection die casting method [10]. The amorphous nature of each alloy was verified on the central section of the casting using X-ray diffraction (XRD) with a Phillips MRD instrument fitted with a focused 0.5-mm micro capillary tube and Cu Kα radiation source. Thermophysical data was determined using a Netzch 204F1 differential scanning calorimeter (DSC) in aluminium pans under a circulating argon atmosphere.

3. Results and discussion

Both the critical casting thickness (Z_C) (using a wedge mould) and diameter (Z_C) (in 0.5 mm increments) were tested for the determined range of glass forming alloy compositions. For all alloys, D_C was larger than Z_C in accordance with the geometric heat transfer relationship (i.e. Z_C (plate) ~ 0.7D_C [11]). The shaded regions in Fig. 1 indicate the BMG formation range of the respective alloy systems. The alloy with the largest critical casting size of the ternary alloys, $Ag_{38.4}Mg_{38.4}Ca_{23.2}$, happens to have the lowest liquidus temperature of the alloys tested and appears to be a ternary eutectic composition.

It is also noted that, with the addition of Cu to the glass-forming ternary alloys, the bulk glass forming range has also shifted to lower Ag concentrations. Indeed, substitution of Cu for either Mg or Ca in alloys containing over 53 at.% Ag showed very poor GFA (i.e. $Z_C < 0.2$ mm) when injection cast. This could also be an effect of a reduction in the average atomic radius of the alloy, or, perhaps the substitution of a larger atom (either Ag, Mg, or Ca) with the smaller Cu atom to the coordination shell of a cluster which will effectively reduce its packing efficiency, resulting in a reduction in GFA [3,4]. Further, the addition of a fourth element of different atomic size to the system effectively creates additional short-range structures/clusters of different atomic centres and may contribute to hindering atomic rearrangement during crystallization, often referred to as the 'confusion principle' [12].

It can be seen in Table 1, particularly for the quaternary alloys, that as the Ag-content is increased, the GFA of the alloys decreases. Thermodynamics aside, this decrease in GFA may be due to a decrease in the average atomic radius of the alloys, where it is known that the rate of crystallization is lower in alloys containing larger atomic species [1,2]. No substantial glass was formed

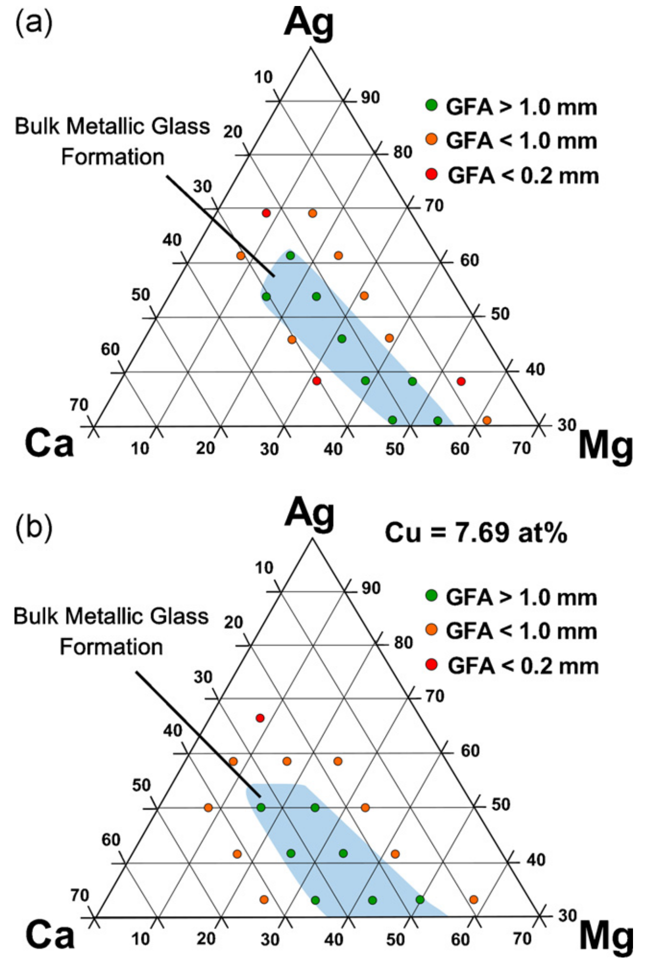

Fig. 1. Alloy composition diagrams indicating bulk metallic glass formation range and the extent of glass formation for: (a) Ag–Mg–Ca ternary system, and (b) Ag–Mg–Ca–Cu quaternary system for a Cu-concentration interval of 7.69 at.%.

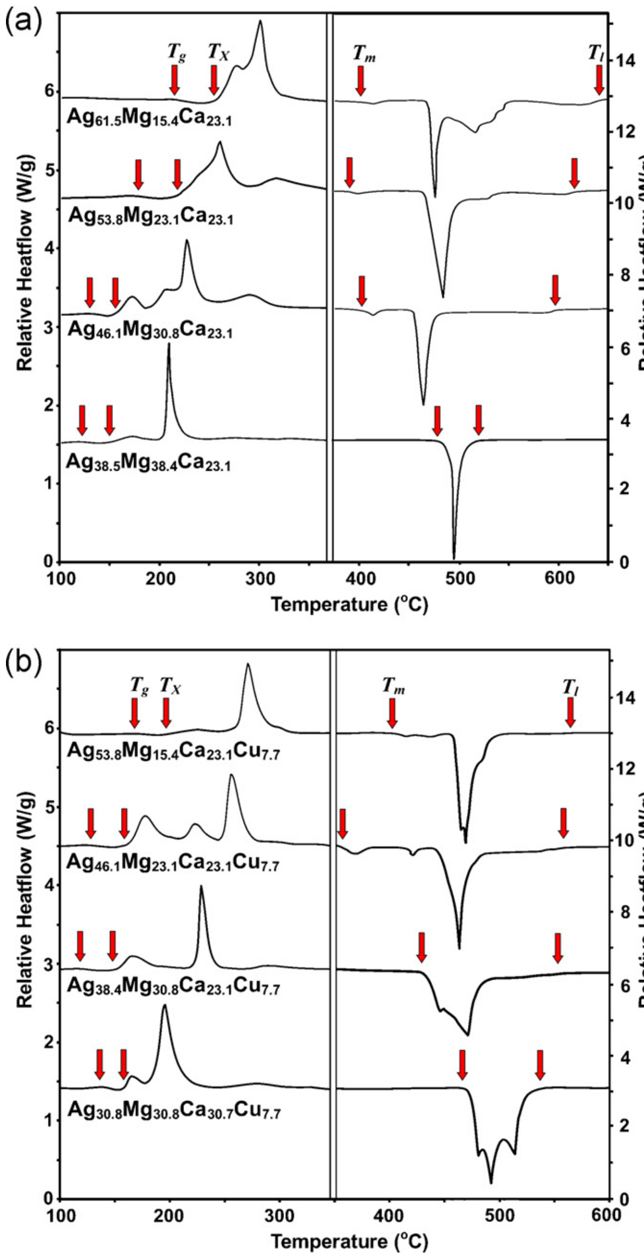

Fig. 2. DSC traces for selected Ag-based BMGs in: (a) Ag–Mg–Ca ternary system, and (b) Ag–Mg–Ca–Cu quaternary system.

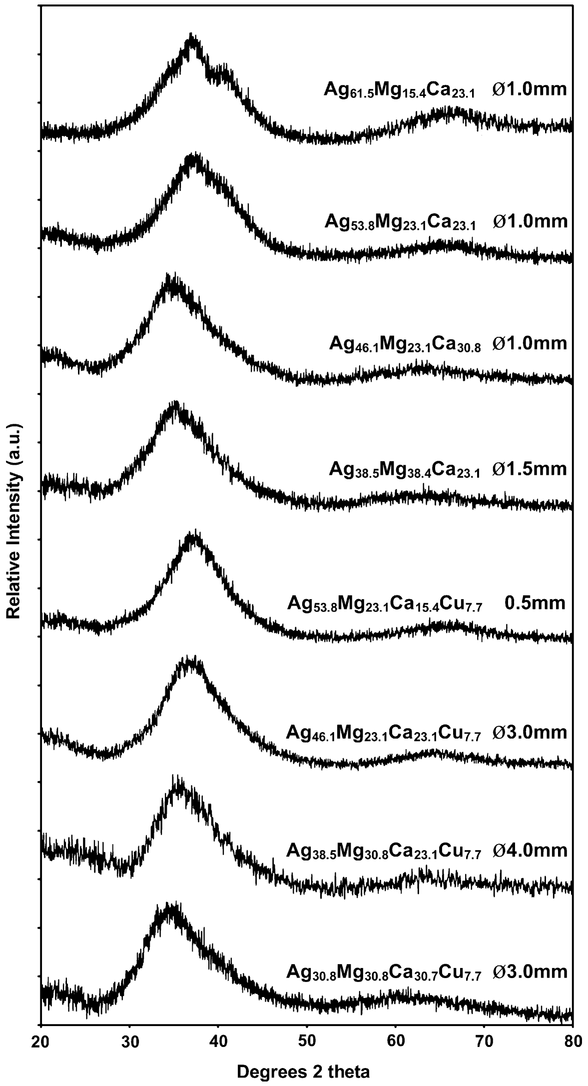

Fig. 3. XRD traces for selected Ag-based BMGs in the Ag–Mg–Ca ternary and Ag–Mg–Ca–Cu quaternary systems.

for $Ag_{69.2}Mg_{7.7}Ca_{23.1}$ and Z_C of only ~0.2 mm was observed for $Ag_{69.2}Mg_{15.4}Ca_{15.4}$ (not shown in Table 1) after injection casting into the wedge mould.

While yet to be reported, it was also recognised that the composition range of efficiently packed clusters also extends into the Mg-rich region of the system, which has been found to form Mg-based BMGs with Mg concentrations as high as 76 at.%. Preliminary work has also shown that the partial substitution of Mg or Ca with rare earth elements that have an intermediate atomic radius of ~180 pm introducing an $N = 15$ efficiently packed configuration also supports and enhances glass-formation in some of these Ag-based alloys.

Fig. 2 shows the DSC traces for selected Ag-based BMGs. These alloys show distinct glass transition behaviour prior to primary crystallization, with glass transition temperatures and supercooled liquid regions generally increasing with increasing Ag and Ca content, which is plausibly due to the higher binding potential between Ag–Ca (followed by Ag–Mg) over other atomic pairs present [13]. No ternary phase diagram or liquidus isosurface has been determined for the Ag–Ca–Mg system, and it can be seen in Fig. 2 that crystallization reactions are broad and varied, with up to four different reactions visible in any given alloy. The multi-stage melting behaviour present in the majority of these alloys are spread over a large temperature range, revealing that the majority of these alloy compositions lie far from eutectic reactions, further highlighting the significant role played by crystallization kinetics in the formation of these glasses. Indeed, the melting range of $Ag_{61.5}Mg_{15.4}Ca_{23.1}$ is 231 °C. The $Ag_{38.4}Mg_{38.4}Ca_{23.2}$ alloy, which has the highest GFA found in these Ag-based alloys, appears to lie on a eutectic reaction with a narrow melting range of 35 °C.

Fig. 3 shows representative XRD traces for selected Ag-based metallic glasses. It is noted in general that, as the Ag content is increased, the peaks of the first and second amorphous halos shift to higher 2θ-values as a result of the increase in Ag–Ag pairs; Ag being smaller in atomic radius than Ca and Mg. It can also be seen that, for the higher Ag-containing ternary alloys, the primary halo changes shape; for the $Ag_{53}Mg_{23}Ca_{23}$ alloy a distinct shoulder begins to appear on the left-hand side of the primary halo and, for the $Ag_{61}Mg_{15}Ca_{23}$ alloy, the halo has split into two peaks which is again thought to be due to the increase in Ag–Ag pairs. A less obvious shoulder also appears on the right-hand side of the primary halo, which is thought to be due to more distinct Ag–Ca pairing and the possible development of longer-range ordering. It is also noted in the $Ag_{61}Mg_{15}Ca_{23}$ alloy that the second halo contribution at $2\theta \sim 67^\circ$ is also considerably higher than the other alloys seen herein, again due to the expected higher number of Ag–Ag pairs and the fact that Ag has a much higher scattering factor than Mg and Ca (where X-ray scattering scales with atomic number).

4. Conclusions

A range of Ag-based BMG-forming alloys were produced by copper mould casting with the potential of having unique functional material properties. The discovery of metallic glasses in the Ag–Mg–Ca–Cu alloy system that contains elements with simplistic, well defined electronic structures over a broad composition range provides a unique opportunity for further investigations into the structural and electronic nature responsible for glass-formation in metal alloys In addition, this work provides further evidence [4,14,15] that bulk amorphous alloys may be produced some distance from deep eutectic reactions in multi-peritectic regions over broad composition ranges.

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