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Development and characterization of Ca–Mg–Zn–Cu bulk metallic glasses

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Abstract

A number of ternary Ca–Mg–Zn and Ca–Mg–Cu and quaternary Ca–Mg–Zn–Cu bulk metallic glasses were produced using recently developed specific criteria. Their glass forming ability was correlated to the alloy chemistry, melting temperature, and driving force for crystallization of super-cooled liquid. A structural assessment using the efficient cluster packing model was also applied and showed a good ability to represent these glasses. Glass transition temperature, crystallization temperature and heat of crystallization were also determined for the produced alloys. Compression tests were conducted on a quaternary alloy at room temperature and in the temperature range of super-cooled liquid.

Keywords: B. Glasses, metallic; B. Phase diagrams; F. Calorimetry; F. Diffraction; F. Mechanical testing

1. Introduction

Ca-based bulk metallic glasses are a relatively new class of amorphous alloys. The first Ca-based glasses were reported by Amiya and Inoue in 2002 [1,2]. They produced fully amorphous rods with a maximum diameter of 4 mm for two ternary alloys, $Ca_{57}Mg_{19}Cu_{24}$ and $Ca_{60}Mg_{20}Ag_{20}$ [1], and 7 mm for a quaternary alloy, $Ca_{60}Mg_{20}Ag_{10}Cu_{10}$ [2]. Later, Senkov and Scott [3,4] analyzed recently developed topological and thermodynamic models of metallic glass formation [5–9] and identified new specific criteria for selection of compositions for good glass forming alloys. By applying these new criteria to Ca-based alloy systems, they predicted that glass formation should be favorable in the alloys described by

$$Ca_A(Y, Ln)_B(Mg, Sn)_C(Al, Ag, Ga, Zn)_D(Cu, Ni, Si)_E \quad (1)$$

where $A = 0.40–0.70$; $B = 0–0.25$; $C = 0–0.25$; $D = 0–0.35$; $E = 0–0.35$, $B + C + D \geq 0.05$ and $A + B + C + D + E = 1$. A strong topological basis [5–9] exists for the compositions represented in Eq. (1), and a structural model has recently been developed following these background developments [10]. This model consists of efficiently packed solute-centered clusters that are themselves densely packed, generally in a face-centered cubic (fcc) arrangement, to efficiently fill space. In addition to the solvent (Ω) and the primary cluster-forming solutes (α), this efficient cluster packing introduces new structural sites at cluster-octahedral (β) and cluster-tetrahedral (γ) positions. If the clusters are packed with fcc symmetry, then the α sites will occupy positions with fcc symmetry in the structure. The β and γ sites occur at the octahedral and tetrahedral positions, respectively, between these α sites. The α solutes are responsible for forming the clusters that comprise the structure, so that α sites are typically filled by α solutes. On the other hand, β and γ sites can be occupied by α, β or γ solutes, or they can be 'vacant'. Vacant β or γ sites are not expected to exist as a single unoccupied volume sufficient to accept an additional solute, but rather is a local concentration of free volume into which Ω atoms may relax, and which may accept an additional solute by rearrangement of these loosely packed Ω atoms into more efficient configurations. A composition range is provided by vacancies or solute anti-site defects on the β or γ sites, and this structural model provides an ability to rationalize compositions for the full range of metallic glasses. A broad assessment of defect states in different metallic glasses has not yet been conducted.

Using new specific criteria and Eq. (1), a number of new Ca-based metallic glasses were produced in ternary (Ca–Mg–Zn, Ca–Sn–Zn, Ca–Mg–Cu, Ca–Mg–Ag, Ca–Mg–Al, Ca–Al–Cu), quaternary (Ca–Mg–Zn–Cu, Ca–Y–Mg–Cu, Ca–Mg–Al–Zn, Ca–Mg–Al–Cu), and quinternary (Ca–Y–Mg–Zn–Cu, Ca–Mg–Al–Ag–Cu, Ca–Mg–Zn–Al–Cu) systems [3,4,11]. These new glasses were produced in the form of 1-mm thick plates to

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validate Eq. (1). The glass forming ability (GFA) as determined by the maximum thickness achievable was not examined. Recently, Park and Kim reported $Ca_{65}Mg_{15}Zn_{20}$ glassy alloy with a maximum diameter of 15 mm produced by copper mold casting in air [12], and Guo, Poon and Shiflet produced Ca–Al–Cu, Ca–Al–Ag, Ca–Mg–Al, Ca–Mg–Al–Cu and Ca–Mg–Al–Ag glasses with a maximum thickness of 2–3 mm [13]. The compositions of all produced Ca-based bulk metallic glasses corresponded to Eq. (1). The breadth of Eq. (1) and the results just cited indicate that many Ca-based alloys are good glass formers.

Ca-based metallic glasses have unique properties [4]. For example, they have low density ($\sim$2.0 g/cm^3), low Young's modulus ($\sim$17–20 GPa) comparable to the modulus of human bones, low glass transition temperature ($T_g \sim 110$ °C) and a wide temperature range of super-cooled liquid ($\Delta T_x = T_x - T_g \sim 30$–70 °C). While most Ca-based crystalline alloys oxidize in air in a matter of days, many Ca-based metallic glasses (i.e. Ca–Mg–Cu, Ca–Mg–Al) have satisfactory oxidation resistance and retain shiny surfaces long after casting. In the present work, the GFA of several Ca–Mg–Zn, Ca–Mg–Cu, and Ca–Mg–Zn–Cu alloys is determined as the maximum thickness at which the alloys are fully amorphous during copper mold casting. The glass transition and crystallization temperatures are also reported for these alloys. The GFA is correlated to the alloy chemistry, melting temperature and driving force for crystallization of super-cooled liquid. A structural assessment based on a recently published structural model for metallic glasses is made, and compositions predicted from this model are compared with the experimental observations. The deformation behavior of the glassy alloys at room and elevated temperatures is also estimated.

2. Experimental procedures

The alloys were prepared by mixing and induction melting of 99.9% pure elements. The prepared alloys were induction re-melted in a quartz crucible and the molten metal was poured from the bottom part of the crucible into a water cooled copper mold with step-like or wedge-like cavities. The step-like samples had 10 mm width and graded thicknesses of 2, 4, 6, 8 and 10 mm. The wedge-like samples had two different configurations; i.e. some samples were 10 mm wide, 50 mm long and their thickness varied from 2 to 10 mm, while other samples were 6 mm wide, 30 mm long and their thickness varied from 0.5 to 3 mm. The samples were cut in pieces of different thicknesses and their amorphous state was examined using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Compression tests were conducted in air on 4-mm diameter $\times$ 8 mm height cast samples using a servo-hydraulic MTS machine.

3. Results and discussion

The amorphous alloy compositions produced in the present work and their maximum thicknesses, τ_m, at which the alloys remain fully amorphous, are given in Tables 1–3. XRD patterns from the alloys with thicknesses at or below τ_m show a wide, diffuse amorphous halo only, indicating a fully amorphous condition; while the XRD patterns from the samples with thicknesses larger than τ_m had both the amorphous halo and sharp peaks from crystalline phases (see Fig. 1a and b). There is a direct relationship between GFA and the maximum thickness [14] so that the alloys with larger τ_m are better glass formers. DSC curves of several amorphous alloys are shown in Fig. 2. The glass transition temperature, crystallization temperature, the temperature range of super-cooled liquid, melting temperature, crystallization exothermic peaks and an endothermic reaction corresponding to melting are clearly identified on

Table 1
Composition, maximum thickness (τ_m), glass transition (T_g), crystallization (T_x), solidus (T_m), and liquidus (T_l) temperatures for Ca–Mg–Zn ternary glassy alloys

Alloy composition	τ_m (mm)	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)
$Ca_{55}Mg_{25}Zn_{20}$	1.0	102	145	336	478
$Ca_{55}Mg_{20}Zn_{25}$	2.0	110	155	350	429
$Ca_{55}Mg_{18}Zn_{27}$	0.5	116	146	350	398
$Ca_{55}Mg_{15}Zn_{30}$	0.5	114	146	350	423
$Ca_{60}Mg_{25}Zn_{15}$	1.0	104	136	336	471
$Ca_{60}Mg_{20}Zn_{20}$	4.0	105	142	336	387
$Ca_{60}Mg_{17.5}Zn_{22.5}$	10.0	110	148	336	377
$Ca_{60}Mg_{15}Zn_{25}$	6.0	106	154	336	377
$Ca_{60}Mg_{10}Zn_{30}$	0.5	107	127	350	393
$Ca_{62.5}Mg_{17.5}Zn_{20}$	10.0	102	139	336	367
$Ca_{65}Mg_{25}Zn_{10}$	0.5	114	132	336	486
$Ca_{65}Mg_{20}Zn_{15}$	5.0	107	132	336	395
$Ca_{65}Mg_{15}Zn_{20}$	6.0	104	137	336	357
$Ca_{65}Mg_{10}Zn_{25}$	2.0	104	139	336	386
$Ca_{70}Mg_{15}Zn_{15}$	0.5	98	124	336	415
$Ca_{70}Mg_{10}Zn_{20}$	0.5	94	126	336	384

Table 2
Composition, maximum thickness (τ_m), glass transition (T_g), crystallization (T_x), solidus (T_m), and liquidus (T_l) temperatures for Ca–Mg–Cu ternary glassy alloys

Alloy composition	τ_m (mm)	T_g (°C)	T_x (°C)	T_m (°C)	T_l (°C)
$Ca_{40}Mg_{30}Cu_{30}$	0.5	122	157	374	421
$Ca_{40}Mg_{25}Cu_{35}$	4.0	126	163	377	407
$Ca_{45}Mg_{30}Cu_{25}$	1.0	128	163	354	444
$Ca_{45}Mg_{25}Cu_{30}$	6.0	127	165	354	405
$Ca_{45}Mg_{19}Cu_{36}$	0.5	126	155	376	441
$Ca_{50}Mg_{30}Cu_{20}$	2.0	129	166	354	458
$Ca_{50}Mg_{25}Cu_{25}$	9.0	127	166	354	382
$Ca_{50}Mg_{20}Cu_{30}$	8.0	128	169	355	417
$Ca_{53}Mg_{23}Cu_{24}$	7.0	133	166	354	382
$Ca_{54}Mg_{18}Cu_{28}$	1.0	126	169	355	418
$Ca_{55}Mg_{20}Cu_{25}$	2.0	126	153	355	447
$Ca_{55}Mg_{10}Cu_{35}$	0.5	124	149	355	497
$Ca_{58}Mg_{18}Cu_{24}$	6.0	115	153	355	394
$Ca_{60}Mg_{25}Cu_{15}$	2.0	117	143	355	403
$Ca_{60}Mg_{20}Cu_{20}$	4.0	114	139	356	405
$Ca_{60}Mg_{13}Cu_{27}$	1.0	121	153	355	428
$Ca_{65}Mg_{25}Cu_{10}$	0.5	132	156	364	418
$Ca_{65}Mg_{20}Cu_{15}$	2.0	113	132	363	406
$Ca_{65}Mg_{15}Cu_{20}$	4.0	110	136	357	409
$Ca_{65}Mg_{10}Cu_{25}$	2.0	115	147	357	438
$Ca_{65}Mg_5Cu_{30}$	0.5	130	151	357	484
$Ca_{70}Mg_{20}Cu_{10}$	0.5	83	112	386	429
$Ca_{70}Mg_{10}Cu_{20}$	1.0	112	134	397	440