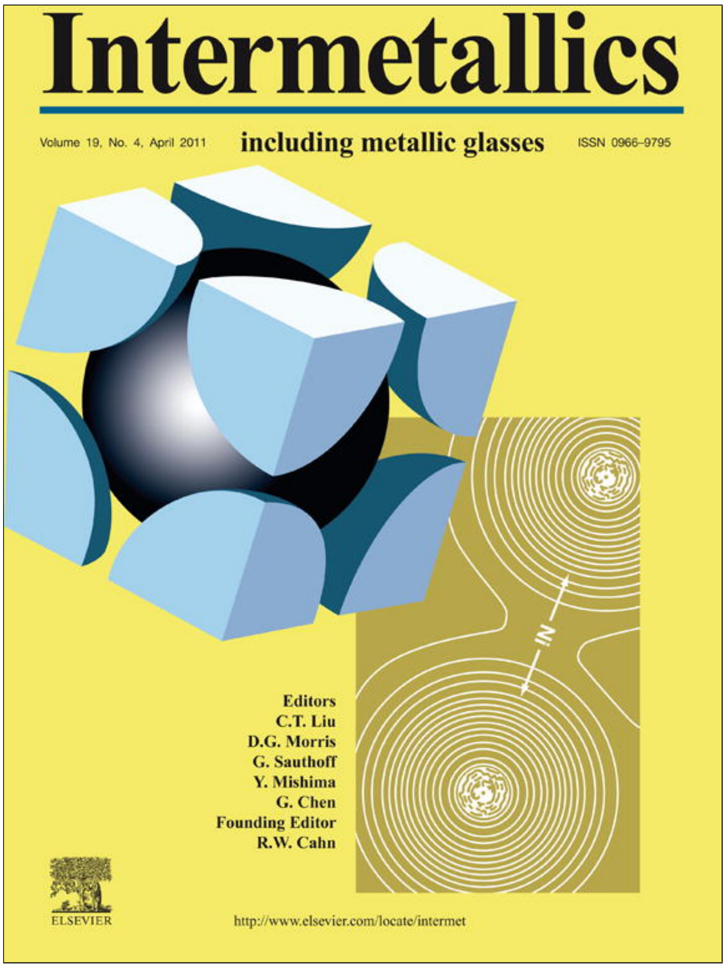
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Fabrication of bulk metallic glasses at the region of multiple quasi-peritectic reactions

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ABSTRACT

We report that Ca-Cu-Mg bulk metallic glasses (BMGs) can be fabricated at the region of multiple quasi-peritectic reactions by a conventional copper mold casting method, demonstrating that finding a deep eutectic composition is not the sole solution for the fabrication of BMGs. Unusual relationship between the glass transition temperature and the elastic constants of these BMGs were discussed in comparison with other BMGs. These results have implications for exploring new BMGs and understanding the glass formation mechanism.

1. Introduction

Bulk metallic glasses (BMGs) as a prominent class of functional and structural materials with a unique combination of properties have been an important part of the materials science scene in the last two decades [1–3]. One of the fundamental issues remained elusive in this field is how to understand the composition dependence of glass-forming ability [4–9]. It is known that a deep eutectic composition is favored for the formation of BMGs, originating from the thermodynamics and kinetics of both liquids and crystalline states [4,10]. However, recently, it has been found that at or near a deep eutectic composition is not the sole region for producing BMGs. For instance, the stoichiometric CuZr compound with a simple B2 structure metastable at ambient conditions, whose composition is far away from deep eutectic of equilibrium phase diagram, is able to be casted into bulk glass by conventional copper mold [10,11]. This B2 phase can be further destabilized by alloying with Al, Ag, Ti, and Be. And thus the critical diameter for Cu-Zr-Me (Me=Al, Ti, Ag and Be), which is an indicator of glass-forming ability, can be improved from 1–2 mm to 5–8 mm in diameter [12–15]. That means BMGs can be fabricated by suppressing the formation of crystalline phases. It is also known that the formation of crystalline phases (β and/or γ) in quasi-peritectic reactions [16] ($L+\alpha\text{——>}\beta+\gamma$) takes place as the dissolving of the primary phase (α) through diffusion in solid state [17], which is more sluggish than in liquids. It is especially the case if the quasi-peritectic reaction appears multiple times during the cooling process. The possibility for BMG formation at this composition region could be increased greatly. Up to now, few such studies have been reported.

In this work, we report that equiatomic CaCu compound with orthorhombic structure can be destabilized by alloying with Mg. We explored this CaCu glass forming alloy system in the vicinity of multiple quasi-peritectic points based on aforementioned assumption. Bulk metallic glasses in 5 mm in diameter were successfully fabricated by conventional mold casting method. The glass-forming ability and thermal stability of the newly developed BMGs are comparable to afore-reported eutectic Ca-Mg-Cu system [18]. The remarkable feature is that the formed bulk peritectic metallic glass do not satisfy the previously reported correlation between the glass transition temperatures and the elastic constants found in other eutectic BMGs [5, 19–21]. This investigation might provide a new avenue for exploring BMG forming alloy systems within off-eutectic range and have implications for understanding the glass formation mechanism.

2. Experimental

We then focused on the BMG forming composition along the equiatomic line which is across the quasi-peritectic point U_1 and adjacent to U_3 (Ref.[22]) as marked in Fig. 1 by alloying Mg atoms to

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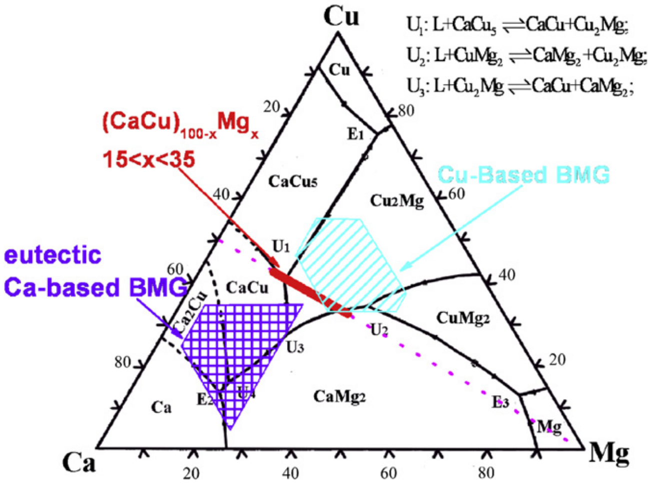

Fig. 1. The location of composition of $(CaCu)_{100\text{-}x}Mg_x$ ($15 \le x \le 35$) alloys in Ca-Cu-Mg ternary phase diagram. (Ref. [22]).

CaCu intermetallic phase. The CaCu intermetallic compound was fabricated by induction melting Ca and Cu (purity better than 99%, 99.9% respectively). (CaCu)-Mg alloys of nominal composition listed in Table 1 were then fabricated by induction melting of CaCu and Mg (purity better than 99.95%) in quartz crucible in a purified argon atmosphere. The alloy melts were finally injected into copper molds to get cylinder shapes. The phase of the as-cast alloy was identified by X-ray diffraction (XRD) using a MAC M03 diffractometer with Cu *Ka* radiation source. Differential scanning calorimetry (DSC) was performed under a purified argon atmosphere in a Mettler Toledo DSC822e with a heating rate of 20 K min^{-1}. The elastic constants (including the Young's modulus E, the shear modulus G, the bulk modus K and Poisson's ratio ν) of the BMGs are derived from the acoustic data and density. The density ρ was measured by Archimedes' principle in deionized water. The acoustic data got from MATEC 6600 ultrasonic system with a measuring sensitive of 0.5 ns, and a carrying frequency of 10 MHz.

3. Results

We developed a series of BMGs in the vicinity of the quasi-peritectic points by alloying Mg to CaCu intermetallic compound. As increasing the content of Mg, the representative XRD patterns of 3 mm cast rods shown in Fig. 2 can be divided into three distinct types according to the as-cast phase. For 10% of Mg addition, the composition is far from the quasi-peritectic reaction point U_3 and deviated from the quasi-peritectic reaction point U_1 as shown in Fig. 1, and its glass-forming ability is limited, there are many sharp crystalline peaks identified as CaCu and CaCu$_5$ intermetallic phase as well as some indistinguishable phase. For further increasing of Mg, when the composition is located at the region of dual quasi-peritectic reactions (as Mg content is 20%, 25% and 30%) that the competitive crystalline counterpart can be fully suppressed and at least 3 mm glassy rods can be produced easily. More Mg addition degrades the glass-forming ability of the alloy as the composition is far from the quasi-peritectic reaction U_1 (Fig. 1). The precipitated competitive crystalline phase is identified as CaMg$_2$ in Fig. 2.

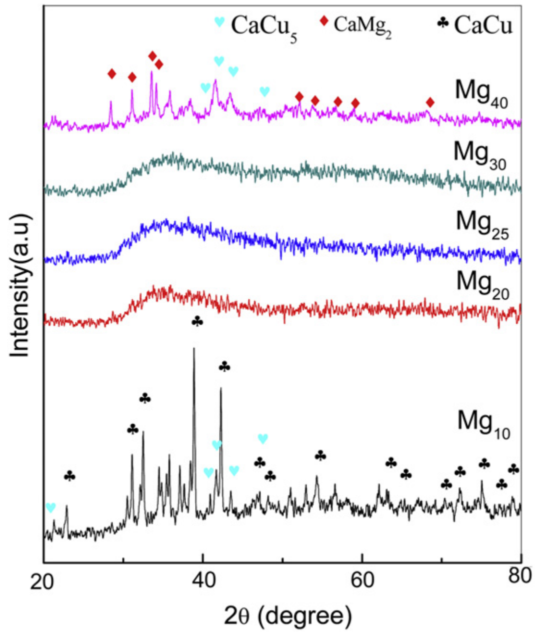

Fig. 2. X-ray diffractograms of 3 mm-diameter as-cast cylinder $(CaCu)_{100\text{-}x}Mg_x$ (x = 10, 20, 25, 30 and 40) alloys.

The glassy nature of above mentioned compositions was also confirmed by DSC curves. The distinct glass transition and sharp crystallization peak during heating with a rate of 20 K min^{-1} of the as-cast $(CaCu)_{100\text{-}x}Mg_x$ (x = 15, 20, 25, 30, and 35) alloys are clearly presented in Fig. 3(a), which further confirm the glass phase of these alloys. The exact values of the glass transition temperature T_g and crystallization temperature T_x are listed in Table 1. Fig. 3 also shows that the BMGs with different Mg contents exhibit different crystallization profiles which indicate that the crystallization behaviors and crystalline products of these BMGs have been altered. This result is in agreement with above XRD results, which shows that the competitive crystalline changed from Ca-Cu intermetallic compound to CaMg$_2$ phase.

The melting curves of the as-cast $(CaCu)_{100\text{-}x}Mg_x$ (x=15,20,25, 30,35) alloys show large difference between the melting temperature T_m and the liquidus temperature T_l as presented in Fig. 3(b) indicating the alloys deviated from the eutectic composition. The exact values of T_m, T_l, reduced glass transition temperature

Table 1
The exact values of the glass transition temperature T_g, crystallization temperature T_x, the melting temperature T_m, liquidus temperature T_l, reduced glass transition temperature T_{rg} ($= T_g/T_l$), γ ($=T_x/(T_g+T_l)$), supercooled liquid region ΔT (T_x - T_g) and the difference between the melting temperature T_m and liquidus temperature T_l ($\Delta T_m = T_l\text{-}T_m$) for CaCu-based peritectic BMGs and eutectic Ca-Based BMGs (Ref.[18]).

Composition	T_g(°C)	T_x(°C)	T_m(°C)	T_l(°C)	T_{rg}	γ	ΔT_x(°C)	ΔT_m(°C)
$(CaCu)_{85}Mg_{15}$	120	149	381	470	0.529	0.253	29	89
$(CaCu)_{80}Mg_{20}$	116	150	377	444	0.542	0.268	34	67
$(CaCu)_{75}Mg_{25}$	115	155	376	433	0.550	0.283	40	57
$(CaCu)_{70}Mg_{30}$	115	138	375	434	0.549	0.251	23	59
$(CaCu)_{65}Mg_{35}$	109	137	378	495	0.497	0.227	28	117
$Ca_{50}Mg_{25}Cu_{25}$	127	166	354	382	0.611	0.326	39	28
$Ca_{50}Mg_{22.5}Cu_{27.5}$	127	169	354	390	0.603	0.327	42	36

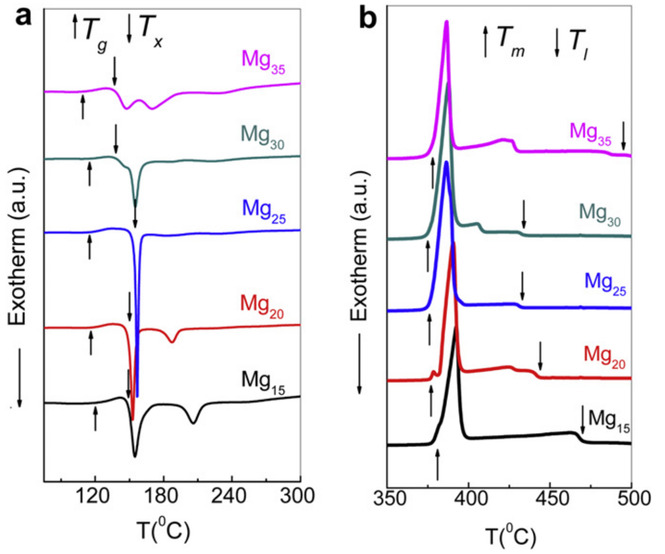

Fig. 3. The DSC curves of the as-cast $(CaCu)_{100-x}Mg_x$ (x = 15, 20, 25, 30 and 35) alloys (a) showing the glass transition and crystallization behaviors. (b) Melting behavior of these BMGs.

T_{rg} ($=T_g/T_l$) [4], γ ($=T_x/(T_g+T_l)$) [7], and supercooled liquid region ΔT_x are also listed in Table 1. The data of Ca-Based eutectic BMG [18] is also listed for comparison. The value of supercooled liquid region ΔT_x of our BMGs is nearly equal to that of the Ca-based eutectic BMG indicating that they have similar thermo stability. Compared to Ca-based eutectic BMGs [18], T_m and T_l of the as-cast $(CaCu)_{100-x}Mg_x$ (x = 15,20,25,30,35) alloys are higher, and the T_{rg} and γ values of $(CaCu)_{100-x}Mg_x$ are smaller. However, $(CaCu)_{75}Mg_{25}$ can be easily cast into glassy rod with a critical diameter of 5 mm, showing high glass-forming ability.

4. Discussion

The composition range of eutectic Ca-Based BMG [18] and our BMG (corresponded to the red line) are marked on the ternary Ca-Cu-Mg phase diagram [22] in Fig. 1, which clearly validates that our BMGs are deviated from the eutectic composition. According to the composition site of Cu-based BMG [23,24] on the ternary Ca-Cu-Mg phase diagram shown in Fig. 1 [22], it is reasonably to infer that the dual quasi-peritectic reactions U_2 and U_3 play an important role for the formation of Cu-based peritectic BMGs.

The $(CaCu)_{70}Mg_{30}$ based on Cu and Ca without main solvent and solute elements compared to other BMGs formed at or near the deep eutectic composition indicates that structure and/or inter-atomic bonding might be different. Elastic moduli, which is sensitive to atomic packing density and interatomic bonding [25], have been found to correlated with glass transition temperatures in metallic glasses [5,19–21]. This relationship can be understood that elastic moduli depend on the atom forming factors and atomic packing efficiency which directly affect the interatomic bonding strength [25,26] and local geometry of atomic clusters [27]. Meanwhile, T_g, scale as bonding strength among atomic clusters or molecules [28], which explains well the observed general trend that glass transition temperature increases with moduli. The elastic constants and T_g of these CaCu-based BMGs and eutectic Ca-based BMGs are measured and listed in Table 2. Compared to the eutectic Ca-based BMGs [29], the values of Young's modulus E, shear modulus G, bulk modus K of these BMGs are much higher while its T_g is relative lower, which is obviously inconsistent with the general relationship between T_g and elastic moduli [5,19–21]. This unusual behavior were also observed in Fe-metalloid based metallic glasses [30], indicating that bonding characters in addition to bonding strength between atomic cluster plays an important role in glass transition. Similar proposal was put forward that covalent bonding exits between the elements in the Ca-Mg-Cu system [18].

Table 2
The elastic constants, density and the T_g for CaCu-based peritectic BMGs and eutectic Ca-Based BMGs (Ref.[29])

Composition	E(GPa)	G(GPa)	K(GPa)	σ	ρ(g cm^{-3})	T_g(°C)
$Ca_{55}Mg_{25}Cu_{20}$	27.98	10.81	22.63	0.294	2.221	125
$Ca_{48}Mg_{27}Cu_{25}$	29.8	12.1	18.4	0.23	2.428	128
$(CaCu)_{75}Mg_{25}$	37.43	14.40	31.1	0.299	3.149	115
$(CaCu)_{70}Mg_{30}$	37.95	14.48	33.3	0.310	3.069	115

5. Conclusion

In summary, we have successfully fabricated CaCu-based BMGs at the region of multiple quasi-peritectic reactions. The obtained bulk peritectic metallic glasses do not satisfy the known correlation between the glass transition temperature and the elastic constants, showing bonding characters in addition to bonding strength between atomic clusters might play an important role in glass transition. The new BMGs with such interesting features enrich the family of BMG, and might have hints for exploring new BMGs and tuning their properties.

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