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Effect of alloy composition on the glass forming ability in Ca-Mg-Zn alloy system

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Abstract

The effect of alloy composition on the glass forming ability (GFA) of the Ca-Zn-Mg alloys has been investigated in the present study. The alloy compositions investigated are near Ca-rich ternary eutectic composition; $Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$, $Ca_{65}Mg_{20}Zn_{15}$, and $Ca_{70}Mg_{15}Zn_{15}$. Bulk metallic glass (BMG) samples with the diameter larger than 5 mm are fabricated by conventional copper mold casting method in air atmosphere. Among the parameters representing the glass forming ability, T_{rg} and γ parameters exhibit good correlation with the maximum diameter of the fully amorphous structure in the alloy compositions investigated in the present study.

1. Introduction

Recently, ternary alloys such as Cu-(Zr, Hf)-Ti [1], Cu-Zr-Al [2], Ni-Nb-(Sn, Ti, Ta) [3-5] and Mg-Cu-(Y, Gd) [6-7] have been reported to require a lower critical cooling rate of 10^0 - 10^2 K/s for the glass formation, thus being able to form bulk metallic glasses (BMGs). These simple ternary alloys can be more suitable for commercial use, and provide a good opportunity for the study of glass-forming mechanisms. So far, most of the BMGs necessitate the fabrication under controlled inert atmosphere in an evacuated closed chamber [8]. However, rapid and simple production techniques can facilitate the wide-spread of BMGs in industrial products. For example, the ternary $Mg_{65}Cu_{25}Gd_{10}$ BMG with diameter of at least 8mm was fabricated by conventional Cu-mold casting method in air atmosphere [7].

Recently, it has been reported that the ternary $Ca_{65}Mg_{15}Zn_{20}$ BMG with diameter of at least 15 mm can be successfully fabricated by conventional copper mold casting method in air atmosphere [9], indicating that the glass forming ability (GFA) of the Ca-Mg-Zn alloy is significantly improved when compared with that of the Ca-Mg-M (M: Cu, Ni, Ag) alloys [10, 11]. It has been also pointed out that the parameters for GFA suggested so far, i.e. ΔT_x (=T_x-T_g, T_x: crystallization onset temperature, T_g: glass transition temperature), T_{rg} (=T_g/ T_m^1, T_m^1: finishing temperature of the melting endotherm), K (=[T_x-T_g]/[T_m^1-T_x]) [12] and γ (=T_x/[T_g+ T_m^1]) [13] parameters are no more appropriate to represent the significantly improved GFA in the Ca-Mg-Zn alloy system when compared with those of the Ca-Mg-M (M: Cu, Ni, Ag) alloys. Since we have reported on the glass forming ability of the alloy with the composition of $Ca_{65}Mg_{15}Zn_{20}$ [9], we investigated the effect of alloy composition on the glass forming ability in the Ca-rich Ca-Mg-Zn system, and the relationship between the parameters for GFA (ΔT_x, T_{rg}, K and γ) and GFA of the alloys in the present study. The alloy compositions investigated ($Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$, $Ca_{65}Mg_{20}Zn_{15}$, and $Ca_{70}Mg_{15}Zn_{15}$) were near Ca-rich ternary eutectic composition, as indicated on the liquidus surface projection (Fig.1). To discuss the effect of the alloy composition on the GFA, variations of the glass transition temperature, the crystallization onset temperature and the onset and finishing temperatures of the melting endotherms with the change of alloy composition were studied by thermal analysis of melt spun amorphous alloys. To evaluate the GFA of the alloys, cone-shaped ingots were prepared by conventional Cu-mold casting method in air atmosphere.

2. Experimental

High purity elements Ca (99.9%), Mg (99.9%) and Zn (99.9%) were alloyed in a graphite crucible in an Ar atmosphere using an induction furnace. After complete melting, the liquid alloy was poured into a copper mold in air atmosphere. The copper mold is cone-shaped with 45 mm in height, 15 mm in diameter at the top, and 5 mm in diameter at the bottom. For comparison, rapidly solidified ribbon samples were prepared by re-melting the appropriate amount of the alloys in quartz tubes followed by ejecting with an over-pressure of 50 KPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons have a thickness of about 45 μm and a width of about 2 mm.

For the structural and thermal analyses, thin slices were cut from the as-cast cone-shaped ingots with different diameters from 5 mm to 15 mm. The surfaces of the thin slices were examined by X-ray diffraction (XRD), with a monochromatic Cu K_α radiation. The thermal analysis of the as-melt-spun ribbons was carried out to determine T_g, T_x, T_m^s (onset temperature of the melting endotherm) and T_m^l by differential scanning calorimetry (DSC), using a heating rate of 0.667 K/s. To carefully confirm the amorphous structure of the cone-shaped ingot, the specimens from the center to the edge of thin slices were examined in the DSC.

3. Results

Figure 2 shows DSC traces obtained from as-melt-spun ribbon samples with the composition of $Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$, $Ca_{65}Mg_{20}Zn_{15}$, and $Ca_{70}Mg_{15}Zn_{15}$ during continuous heating with a heating rate of 0.667 K/s. All the samples exhibited a distinct glass transition, followed by a broad super-cooled liquid region and then exothermic reactions due to crystallization. Table 1 summarizes the results of the thermal analysis (T_g, T_x, T_m^s and T_m^l) for the alloys investigated in the present study. Table 1 also includes the parameters for glass forming ability, i.e. ΔT_x, T_{rg}, K and γ. The glass transition and crystallization onset temperatures of the alloys investigated were in the range of 371 - 382 K and 389 - 426 K, respectively. The onset temperatures of the melting endotherms for the alloys investigated were almost same, i.e. in the range of 609 - 612 K. However, the range of the melting endotherms varies from 12 K to 77 K with the change of alloy composition. The $Ca_{65}Mg_{15}Zn_{20}$ alloy has a single melting endothermic peak with a small melting range of about 12 K, indicating that the alloy composition is close to the ternary eutectic composition [14].

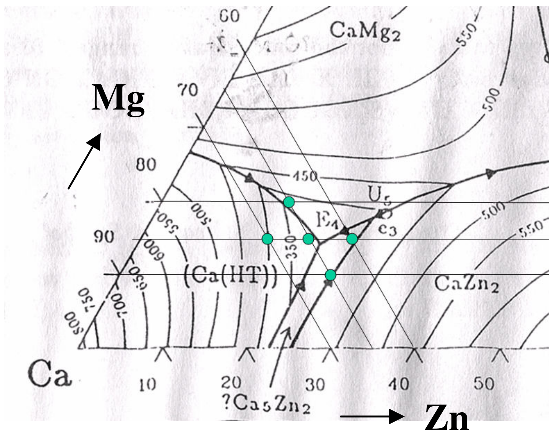

Fig 1. Schematic diagram of near Ca-rich ternary eutectic compositions investigated in the present study

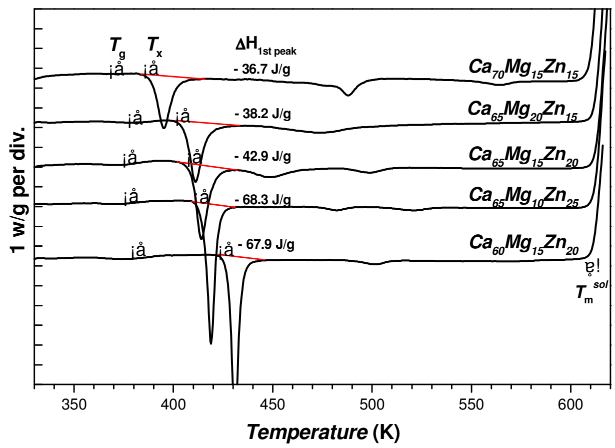

Fig 2. DSC traces of rapidly solidified Ca-Mg-Zn alloy ribbons obtained during heating with a heating rate 0.667 K/s

To evaluate the GFA with changing the alloy composition, the thin slices cut from the cone-shaped ingot with the diameters were investigated by XRD and DSC. The maximum diameter for the fully amorphous structure in each alloy composition is included in Table 1. Among the alloys investigated, the alloy with the composition of $Ca_{65}Mg_{15}Zn_{20}$ exhibited the highest glass forming ability enabling to form BMG sample with the diameter of at least 15 mm. The amorphous structure of the injection-cast ingot was carefully examined by DSC and XRD (not shown) [9].

Table 1. The results of thermal analysis (T_g, T_x, T_m^s and T_m^l), parameters for GFA (ΔT_x, K, T_{rg}, and γ) and maximum diameter for fully amorphous phase formation (D_{max}, mm) for Ca-Mg-Zn alloys

Alloys	T_g (T/K)	T_x (T/K)	T_m^s (T/K)	T_m^l (T/K)	ΔT_x (T/K)	K	T_{rg}	γ	D_{max}(mm)
$Ca_{60}Mg_{15}Zn_{25}$	382	426	612	676	44	0.176	0.565	0.403	11
$Ca_{65}Mg_{10}Zn_{25}$	378	414	612	686	36	0.132	0.551	0.389	6
$Ca_{65}Mg_{15}Zn_{20}$	379	412	612	624	33	0.156	0.607	0.411	15
$Ca_{65}Mg_{20}Zn_{15}$	380	405	612	666	25	0.096	0.571	0.387	9
$Ca_{70}Mg_{15}Zn_{15}$	371	389	609	686	18	0.060	0.541	0.368	5

4. Discussion

Present study shows that the Ca-Mg-Zn alloys near the Ca-rich ternary eutectic composition exhibit high glass forming ability. The alloy with the composition of $Ca_{65}Mg_{15}Zn_{20}$ exhibits the highest glass forming ability enabling to form BMG sample with the diameter of at least 15 mm. The high glass forming ability in the Ca-Mg-Zn alloy system can be explained by the empirical rules: (1) large atomic size difference between the alloy elements (Ca: 1.97 Å; Mg: 1.60 Å; Zn: 1.38 Å); (2) large negative mixing enthalpy between the alloy elements (Ca-Mg: -20 J/mol; Ca-Zn: -72 J/mol; Mg-Zn: -13 J/mol); and (3) existence of a deep ternary eutectic reaction in the Ca-rich composition range [14]. The decrease in melting point indicates that the liquid phase is stabilized with respect to competing crystalline phases. The stabilization of the liquid phase can be also achieved by increasing the atomic packing density in the liquid phase. A large atomic size difference between constituent elements is favorable to increase the atomic packing density of the liquid structure. The larger enthalpies of mixing can contribute to the stabilization of the liquid phase by changing the local atomic structure.

It is known that cooling rate is inversely proportional to the diameter of ingot. Therefore maximum diameter for amorphous formation can be considered as a real parameter reflecting glass forming ability of the alloy. Figure 3 shows correlations between the suggested parameters, ΔT_x, K, T_{rg} and γ, and maximum diameter for amorphous phase formation in the Ca-Mg-Zn alloys investigated in the present study. In this alloy system, super cooled liquid region, ΔT_x, and K parameter do not show good relationship with the measured maximum diameter of amorphous specimen. However, reduced glass transition temperature, T_{rg} and γ parameter exhibit good correlation with the maximum diameter. The high glass forming ability in Ca-Mg-Zn alloy seems to be related with the existence of a deep ternary eutectic reaction in the Ca-rich composition range.

The present results indicate that among the parameters suggested for GFA, T_{rg} and γ parameters properly represent the GFA of the Ca-Mg-Zn alloys. However, when compared with the T_{rg} and γ parameters and GFA of the Ca-Mg-M (M: Cu, Ni, Ag) alloys [10,11] (for example; γ values for $Ca_{57}Mg_{19}Cu_{24}$ (D_{max}: 4 mm)[10], $Ca_{60}Mg_{20}Ag_{20}$ (D_{max}: 4 mm)[11] and $Ca_{70}Mg_{15}Zn_{15}$ (D_{max}: 5 mm) are 0.425, 0.412 and 0.397 [Here, T_m^s was used to compare the γ value with those reported in the previous study], respectively, although the GFA of the alloys is similar), the parameters do not properly represent of the higher GFA in Ca-Mg-Zn alloys than that in the Ca-Mg-M (M: Cu, Ni, Ag) alloys.

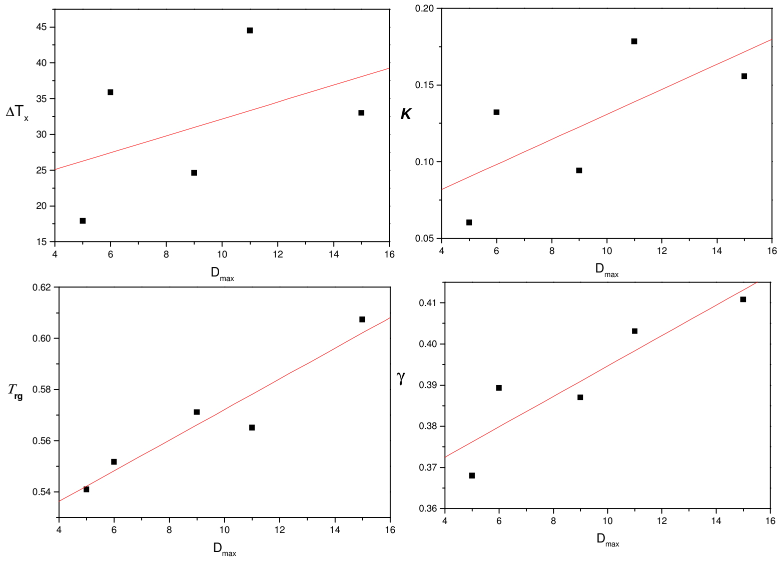

Fig 3. Correlations between the suggested parameters, ΔT_x, K, T_{rg} and γ, and maximum diameter for amorphous formation in the Ca-Mg-Zn alloys investigated in the present study

5. Summary

The glass forming ability of the alloys with the compositions of near ternary eutectic composition ($Ca_{60}Mg_{15}Zn_{25}$, $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{65}Mg_{15}Zn_{20}$, $Ca_{65}Mg_{20}Zn_{15}$, and $Ca_{70}Mg_{15}Zn_{15}$) is investigated. Ca-based bulk metallic glass (BMG) samples with the diameter larger than 5 mm are fabricated by conventional copper mold casting method in air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest glass forming ability enabling to form BMG sample with the diameter of at least 15 mm. When compared with the GFA of Ca-Mg-M (M: Cu, Ni and Ag) alloys, the significant improved GFA of the Ca-Mg-Zn alloy cannot be represented by ΔT_x, T_{rg}, K and γ parameters. However, T_{rg} and γ parameters exhibit good correlation with the maximum diameter in the Ca-Mg-Zn alloys investigated in the present study.

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